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R12 METHODS, GAUSSIAN GEMINALS

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The basis-set truncation error of standard electron-correlation treatments represents a serious problem in computational chemistry. Wavefunction models that are restricted to products of one-particle basis functions – that is, the orbital approximation – converge very slowly to the true solutions that would be obtained in a complete basis. The convergence of the orbital approximation can be characterized as N^{-1}, where N is the number of functions in the correlation-consistent basis. Extrapolation schemes appear to help to overcome this basis-set convergence problem and even more so do expansions that not only employ one-particle basis functions, but also basis functions that depend on the coordinates of more than one electron. R12 methods and Gaussian geminals employ two-electron basis functions that depend on the interparticle distance r_{12}. In more general explicitly correlated Gaussians (ECG) also functions that depend on the coordinates of more than two electrons occur. The present discussion of the various many-electron basis functions focuses on methods that can be applied to molecular many-electron systems and is less concerned with highly accurate calculations of atomic electronic structure.

1 Introduction

R12 methods, Gaussian geminals, and explicitly correlated Gaussians have been introduced to computational quantum chemistry with the purpose to facilitate calculations of dynamical electron-correlation effects and have in common that they include the interparticle distances r_{ij} into the many-electron wavefunction.

It had been recognized already in the early days of quantum mechanics that the electron-electron distance r_{12} ought to be included into the wavefunction if quantitatively accurate computational results were to be obtained[1–6]. In 1937, Hellmann wrote about the electron-correlation effect[4]:

> *Der Effekt spielt bei allen feineren quantitativen Rechnungen eine große Rolle, ist aber meist schwer rechnerisch zu erfassen, da er die Einführung von r_{12} in die Eigenfunktion erfordert.*

(The correlation effect plays an important rôle in all precise quantitative calculations but is mostly difficult to describe computationally, as it requires the inclusion of r_{12} into the wavefunction.) Indeed, as we will see later in the present lecture notes, the accurate computation of the dynamical electron-correlation effects is very difficult with the standard electron-correlation treatments[7,8] within the orbital approximation – that is, treatments that are based on wavefunction expansions in terms of antisymmetrized orbital products (Slater determinants). These calculations are difficult in the sense that the computed electronic energies and molecular

properties are very dependent on the orbital basis sets used. When larger and larger basis sets are used, the computed data keep changing and converge only very slowly to the limiting value of an infinitely large, complete basis set. In particular, the convergence is so slow that the computational costs of the correlated calculations grow four orders of magnitude faster than the rate with which the basis-set truncation errors decrease. In order to reach the next level of accuracy, which corresponds to a reduction of the truncation error by a factor of ten, calculations are required that consume roughly 10000 times more computing time. We will see that, as a function of the error δ, the required computing time of standard electron-correlation treatments can be expressed as:

$$t_{\mathrm{cpu}}(\delta) = \delta^{-4}. \tag{1}$$

This means in practice that if we want to improve (by one order of magnitude) certain calculations that take something like one minute of computing time on a given computer, we have to perform calculations that run for a whole week on that same computer. We would have to wait almost 200 years to achieve results at the next level of accuracy! Evidently, the scaling of standard *ab initio* electronic-structure calculations in terms of the basis-set truncation error is nothing else but disastreous.

In the present lecture, we will be concerned with computational approaches that address this slow basis-set convergence and the corresponding scaling problems.

2 Errors in electronic-structure calculations

What precisely are the errors we are dealing with when we perform electronic-structure calculations? It is of course important to ask this question and especially to find out about the most significant sources of error in our calculations. If more accurate calculations are required, that is, if more reliable computational data are needed, one can then focus on the most important sources of error and address these.

In *ab initio* electronic-structure calculations, approximate solutions are obtained to the nonrelativistic electronic Schrödinger equation in the framework of the Born-Oppenheimer (BO) approximation. We can thus define the errors of our *ab initio* calculations relative to the true solutions of that equation, and that is what we will do in the following. This implies that we will not be concerned with relativistic or non-BO effects. There are cases, of course, where these effects become important, but we will restrict our discussion to the nonrelativistic BO case. Clearly, it depends on the level of accuracy we are aiming at whether relativistic or non-BO effects should be taken into account. Table 1 shows the order of magnitude of these effects on electronic barriers in the H_2O and SiH_3^- molecules. When aiming at an accuracy of about ± 50 cm^{-1} (± 0.6 kJ mol^{-1}), as in the cited works[9,10], it becomes mandatory to include these effects. Scalar relativistic effects and spin-orbit interactions become certainly very important for molecular systems containing heavy elements. We will not discuss this topic further, although it must be said that the basis-set convergence of relativistic calculations is even slower – in fact, significantly slower[11] – than in the nonrelativistic case, implying that explicitly

Table 1. Barrier to linearity of H_2O [a,b] and barrier to inversion of SiH_3^-.[c,d]

	$\Delta E/cm^{-1}$	
	H_2O	SiH_3^-
Nonrelativistic BO-value	11086	8314
Relativistic correction	58	50
Diagonal BO-correction	−17	−13
Total	11127	8351

a C_{2v}: $R_{O-H} = 95.885$ pm, $\angle_{H-O-H} = 104.343°$.[9]
b $D_{\infty h}$: $R_{O-H} = 93.411$ pm.[9]
c C_{3v}: $R_{Si-H} = 153.753$ pm, $\angle_{H-Si-H} = 95.196°$.[10]
d D_{3h}: $R_{Si-H} = 147.641$ pm.[10]

correlated methods would be very powerful in particular in relativistic electronic-structure calculations.

In any case we define[12,13] the *apparent error* as the difference between the true solution of the electronic Schrödinger equation (equal to the experimental value of the property of interest if relativistic and non-BO effects can be neglected) and the particular calculation that we carry out. This apparent error can be subdivided into the *basis-set error* and the *n-electron error*, as our calculation will employ a truncated one-electron basis set and a truncated n-electron wavefunction model. Thus, two approximations are introduced, leading to two sources of error to our computed data. These two errors (basis-set error and n-electron error) depend on the basis set used. In the limit of a complete basis, the basis-set error vanishes and only the n-electron error remains. This remaining n-electron error at the limit of a complete basis is denoted as the *intrinsic error* of the respective n-electron wavefunction model.

We will only be concerned with the basis-set error in the present lecture.

3 The basis-set error

3.1 Correlation-consistent basis sets

The development of the correlation-consistent basis sets (cc-pVXZ) by Dunning and co-workers[14−19] has prompted a series a studies of the basis-set dependence of computed molecular properties in terms of these basis sets. The basis sets are characterized by the *cardinal number* X, and basis sets for $X = 2, \ldots, 6$ have been derived, also in the aug-cc-pVXZ[15] and cc-pCVXZ[18] forms. The latter two series of basis sets are cc-pVXZ sets to which diffuse, respectively tight Gaussians have been added. Also aug-cc-pCVXZ basis sets exist as well as doubly augmented sets, and so on.

A typical example of a correlation-consistent basis-set convergence study is shown in Table 2, which shows the all-electron correlation energy of the H_2O molecule at the CCSD(T) level[20,21]. Empirically, as shown in Figure 1, one finds

Table 2. All-electron correlation energies (in E_h) of the H_2O molecule[a].

Basis	N[b]	E_{SCF}	ΔE^c_{MP2}	ΔE^d_{CCSD}	$\Delta E^e_{CCSD(T)}$
Orbital basis					
cc-pCVDZ	28	−76.0272	−0.2413	−0.0104	−0.0033
cc-pCVTZ	71	−76.0574	−0.3175	−0.0067	−0.0082
cc-pCVQZ	144	−76.0649	−0.3426	−0.0039	−0.0095
cc-pCV5Z	255	−76.0671	−0.3516	−0.0018	−0.0100
cc-pCV6Z[f]	412	−76.0673	−0.3563	−0.0005	−0.0102
R12 basis[20] O:15s9p7d5f3g1h/ H:9s7p5d3f1g	320	−76.0674	−0.3615	0.0015	−0.0100

a H_2O geometry: $R_{O-H} = 1.80885\ a_0$, $\angle_{H-O-H} = 104.52°$.[20]

b Number of basis functions.

c Total second-order correlation energy. The MP2-R12 calculations were based on standard approximation B.

d CCSD increment, $E_{CCSD} - E_{MP2}$.

e Triples contribution, $E_{CCSD(T)} - E_{CCSD}$.

f Not available in basis set library[18]. Constructed in analogy to the smaller sets[21].

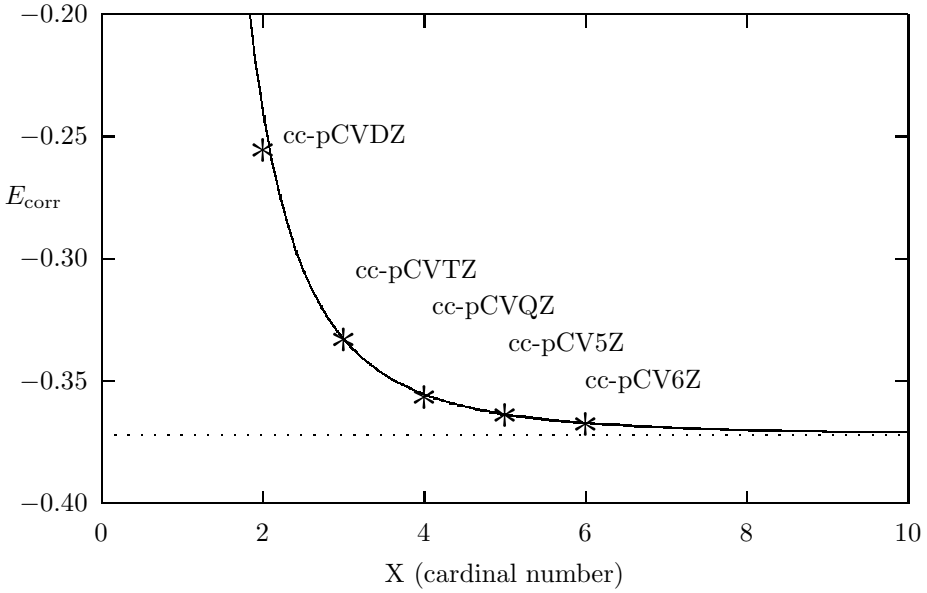

Figure 1. All-electron CCSD(T) correlation energy (in E_h) of the water molecule as a function of the cc-pCVXZ basis sets. Cf. Table 2.

that the cc-pCVXZ results are well represented by the formula:

$$E_{corr}(X) = E_{corr}(\infty) + c\,X^{-3}. \qquad (2)$$

The actual curve in Figure 1 corresponds to $E_{\rm corr}(\infty) = -0.372\ E_{\rm h}$ and $c = 1.07\ E_{\rm h}$. Equation (2) provides an estimate for the basis-set error as a function of X. This basis-set error is equal to $c\,X^{-3}$, and thus, if we would like to reduce the basis-set error of our standard CCSD(T) calculation of H_2O to below 1 m$E_{\rm h}$, we ought to use basis sets with cardinal numbers $X\rangle 10$. Such basis sets do not exist, however. We note in passing that also in the case of the above-mentioned barrier to linearity of the H_2O molecule one finds that a ridiculously large (1276 functions) basis set with $X = 10$ ought to be used to compute the nonrelativistic BO barrier accurate to within 10 cm^{-1}.[9]

Furthermore, we note that the number of basis functions in a cc-pVXZ basis set grows with the third power of X. For first-row atoms, the number is:

$$N = \frac{1}{3}(X+1)(X+\frac{3}{2})(X+2). \tag{3}$$

This cubic dependence implies that we can represent the computed correlation energies obtained with correlation-consistent basis sets alternatively as[22,23]:

$$E_{\rm corr}(N) = E_{\rm corr}(\infty) + c'\,N^{-1} + \mathcal{O}(N^{-2}). \tag{4}$$

It must be said, however, that the latter equation is only correct for the "magic" numbers N that correspond to a correlation-consistent hierarchy of basis sets.

The number of two-electron integrals grows with the fourth power of the number of basis functions, and thus, also the computing time will grow as N^4 when the basis set is enlarged. In the light of this scaling, (1) thus follows from (4). Note that the N^4-scaling refers to an increase of the number of functions per atom. Correlation treatments are being developed that scale linearly with the size of the system[24–26], but from that perspective, the whole molecular system is increased while the number of functions per atom remains constant. Intregral-screening techniques are of little help to the N^4-scaling problem when we enlarge only the basis set per atom.

3.2 Principal expansion

For the ground state of the He atom, it is empirically found that the energy contribution of an individual natural orbital is almost completely independent from its angular momentum and magnetic quantum numbers and only proportional to the inverse sixth power of its principal quantum number n:[27,28]

$$\Delta E_{n\ell m} = -A\left(n-\frac{1}{2}\right)^{-6}. \tag{5}$$

On itself, the observation that the natural orbital increments are proportional to n^{-6} is a strong motivation for the development of hierarchies of basis sets in terms of the principal quantum number n, as is the case for the cc-pVXZ sets. We will denote such an expansion as *principal expansion*. The basis set on a given atom is then defined by some principal quantum number $n_{\rm max} = X$ and all shells of orbitals $\chi_{n\ell m}$ up to that quantum number are included in the principal expansion.

For a calculation that includes only shells with principal quantum number $n \leq X$, the truncation error δE_X is obtained by summing all increments $\Delta E_{n\ell m}$ for

those orbitals not included in the expansion:

$$\delta E_X = \sum_{n=X+1}^{\infty} \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} |\Delta E_{n\ell m}|. \tag{6}$$

The summation can be carried out in closed form and expressed in terms of the polygamma function $\Psi(n,x)$, but replacing the summation over n by integration leads immediately to the same leading X^{-3}- and X^{-4}-terms:

$$\begin{aligned}
\delta E_X &= A \sum_{n=X+1}^{\infty} n^2 \left(n-\frac{1}{2}\right)^{-6} \\
&= \frac{A}{6}\Psi(3,X+\frac{1}{2}) - \frac{A}{24}\Psi(4,X+\frac{1}{2}) + \frac{A}{480}\Psi(5,X+\frac{1}{2}) \\
&= \frac{A}{3}X^{-3} + \frac{A}{4}X^{-4} - \frac{7A}{60}X^{-5} + \mathcal{O}(X^{-6}), \qquad (7) \\
\delta E_X &\approx A \int_{X+\frac{1}{2}}^{\infty} n^2 \left(n-\frac{1}{2}\right)^{-6} dn = \frac{A}{3}X^{-3} + \frac{A}{4}X^{-4} + \frac{A}{20}X^{-5}. \qquad (8)
\end{aligned}$$

In a similar fashion, we can compute the truncation error δE_L of a partial-wave expansion that includes all contributions up to $\ell \leq L$:

$$\begin{aligned}
\delta E_L &= \sum_{n=L+2}^{\infty} \sum_{\ell=L+1}^{n-1} \sum_{m=-\ell}^{\ell} |\Delta E_{n\ell m}| \\
&= \frac{A}{6}\Psi(3,L+\frac{3}{2}) - \frac{A}{24}\Psi(4,L+\frac{3}{2}) - \frac{A}{120}(L^2+2L+\frac{3}{4})\Psi(5,L+\frac{3}{2}) \\
&= \frac{2A}{15}(L+1)^{-3} + \frac{A}{4}(L+1)^{-4} + \frac{2A}{15}(L+1)^{-5} + \mathcal{O}\left((L+1)^{-6}\right), \qquad (9) \\
\delta E_L &\approx A \int_{L+\frac{3}{2}}^{\infty} \left[n^2-(L+1)^2\right] \left(n-\frac{1}{2}\right)^{-6} dn \\
&= \frac{2A}{15}(L+1)^{-3} + \frac{A}{4}(L+1)^{-4} + \frac{A}{20}(L+1)^{-5}. \qquad (10)
\end{aligned}$$

For variational calculations on He, the expression (10) for the basis-set error of the partial-wave expansion has been found empirically[28]. Hill has shown how the coefficients can be derived from the exact He ground-state wavefunction[29] and a very similar expression was derived nearly 40 years ago by Schwartz for the partial-wave expansion in the framework of perturbation theory[30,31]. Kutzelnigg and Morgan have shown that similar rates of convergence apply to many-electron atoms as well[32,33].

It is remarkable that no such analysis exists for the principal expansion, but since the working assumption (5), which is supported by strong numerical evidence, leads to the correct expression for the basis-set error of the partial-wave expansion, it is safe to assume that the basis-set error of the principal expansion is given by (8). This is also supported by the observation that the basis-set error of molecular calculations appears to vanish as X^{-3} with the cardinal number of the correlation-consistent basis sets (cf. Figure 1) and by the fact that extrapolations based on the X^{-3}-form (2) work so well, as we will see in the next section.

Table 3. Statistical measure of errors for all-electron CCSD(T) atomization energies relative to experiment[a]. All values in kJ mol^{-1}.

	Raw cc-pCVXZ results				
	2	3	4	5	6
Δ	−103.07	−34.00	−13.46	−6.61	−4.06
$\Delta_{\rm std}$	37.19	13.58	5.64	3.09	2.14
$\bar{\Delta}_{\rm abs}$	103.07	34.00	13.46	6.61	4.06
$\Delta_{\rm max}$	155.71	51.58	20.15	10.71	7.04
	cc-pCV[(X-1)X]Z extrapolated				
		23	34	45	56
Δ		−14.67	−0.23	0.08	−0.44
$\Delta_{\rm std}$		8.39	2.16	1.12	1.05
$\bar{\Delta}_{\rm abs}$		14.74	1.68	0.90	0.84
$\Delta_{\rm max}$		29.53	4.01	2.45	2.31

a The experimental atomization energies were corrected for (anharmonic) zero-point vibrational energies and (scalar and spin-orbit) relativistic effects.

3.3 Extrapolation schemes

Recently, Bak *et al.*[13,34] applied two-point extrapolations of the form[35]:

$$E_{\rm corr}(X) = E_{\rm corr}(\infty) + cX^{-3} \tag{11}$$

to the CCSD(T)(FULL)/cc-pCVXZ atomization energies of the following 16 closed-shell molecules: CH_2 ($\tilde{a}\ ^1A_1$ state), CH_4, NH_3, H_2O, HF, C_2H_2, C_2H_4, HCN, N_2, CO, H_2CO, HNO, H_2O_2, F_2, CO_2, and H_2. Table 3 shows the mean error ($\bar{\Delta}$), standard deviation ($\Delta_{\rm std}$), mean absolute error ($\bar{\Delta}_{\rm abs}$), and maximum error ($\Delta_{\rm max}$) of the raw CCSD(T)(FULL)/cc-pCVXZ calculations of these molecules in comparison with the two-point extrapolations. The two-point extrapolations are based on calculations with two subsequent basis sets with cardinal numbers $X-1$ and X. For example, the extrapolation denoted as "56" refers to the results that were obtained by inserting the CCSD(T)(FULL)/cc-pCV5Z and CCSD(T)(FULL)/cc-pCV6Z correlation energies into (11) and extracting $E_{\rm corr}(\infty)$ from the two equations with two unknowns. Note that this extrapolation only applies to the electron-correlation contribution to the atomization energy. It was not clear how to extrapolate the Hartree-Fock energy[36] (which perhaps converges exponentially)[37] and thus the Hartree-Fock energy of the larger of the two basis sets was taken.

The extrapolation appears to work! The results displayed in Table 3 show that all errors are significantly reduced by applying the two-point extrapolation. At the raw CCSD(T)(FULL)/cc-pCV6Z level, the mean absolute error is still as large as 4.06 kJ mol^{-1}. We usually refer to an accuracy of about 4 kJ mol^{-1} (or 1 kcal mol^{-1}) as "chemical accuracy". This chemical accuracy is clearly achieved already at the 34-extrapolated level, where the mean absolute error is only 1.68 kJ mol^{-1}. At the 45- and 56- extrapolated levels, the mean absolute errors are 0.90 and 0.84 kJ mol^{-1} and these errors are good estimates of the intrinsic errors of the

Table 4. Application of the two-point (X-1,X)-extrapolation to the MP2(FC) correlation contribution (in kJ mol^{-1}) to the interaction energy of the H_2O dimer in the Halkier geometry[41].

	Raw results[a]	(X-1,X) Extrapolation
aug-cc-pVDZ	−3.35	
aug-cc-pVTZ	−4.78	−5.38
aug-cc-pVQZ	−5.33	−5.74
aug-cc-pV5Z	−5.54	−5.75
Schütz *et al.*[42]		−5.74[b]
R12 result[43]		−5.78

a Within the full counterpoise framework.

b Original value transferred to Halkier geometry[41].

CCSD(T)(FULL) atomization energies.

The two-point X^{-3}-extrapolation has also been tested on reaction enthalpies[13,34], weak interactions[38], spectroscopic constants[39], and dipole moments[40], all with encouraging results. As an example, consider the MP2(FC) contribution to the interaction energy of the H_2O dimer in the fixed geometry optimized by Halkier *et al.*[41] (cf. Table 4). Already the extrapolation from the aug-cc-pVDZ and aug-cc-pVTZ data provides a significant improvement over the raw aug-cc-pVTZ results. The extrapolation is comparable to the aug-cc-pVQZ level. The extrapolation from the aug-cc-pVTZ and aug-cc-pVQZ basis sets virtually coincides with very large calculations by Schütz *et al.*[42] (using more than 1000 basis functions up to $\ell = 7$) and R12 calculations[43]. It must be noted, however, that the extrapolations only work well when applied to the counterpoise-corrected raw data. In general, the extrapolations can be expected to work only when the basis-set error is solely due to the slow convergence of the Coulomb cusp – that is, other basis-set errors such as the basis-set superposition error must be taken care of otherwise. The poor description of the electron-electron cusp must be the only remaining basis-set error. Also in case of the extrapolation of the dipole moments, for example, it was important to use aug-cc-pVXZ basis sets, as the extrapolation is unable to account for missing diffuse functions.

An important feature of the two-point X^{-3}-extrapolation is that it can in principle be applied to any point on the molecular potential energy hypersurface. It is possible to define a model chemistry on the basis of calculations with two basis sets in conjunction with the corresponding two-point X^{-3}-extrapolation. One can optimize molecular geometries and compute harmonic vibrational frequencies within the particular model chemistry[44−47]. Of course, one must be able to separate the Hartree-Fock and correlation contributions, because the extrapolation applies to the (dynamical) correlation energy only. This separation is not always clear-cut on every point on the hypersurface, but maybe one can use an appropriate MCSCF energy as a reference.

Furthermore, we note that in the past other extrapolations from correlation-consistent basis sets have also been tried[12,48−52]. These include the exponential

form[48,52]:

$$E(X) = E(\infty) + a\,\exp(-bX), \tag{12}$$

and the functional forms[49−51]:

$$E(X) = E(\infty) + a\left(X + \frac{1}{2}\right)^{-4}, \tag{13}$$

$$E(X) = E(\infty) + b\left(X + \frac{1}{2}\right)^{-4} + c\left(X + \frac{1}{2}\right)^{-6}, \tag{14}$$

$$E(X) = E(\infty) + d\left(X + \frac{1}{2}\right)^{-e}. \tag{15}$$

It is clear, however, that the exponential form overestimates the rate of convergence of the correlation energy obtained with the correlation-consistent basis sets. Moreover, the leading term is clearly X^{-3}.

All of the above extrapolations were mainly concerned with the (correlation) energy. The basis-set convergence of molecular properties might of course be different from the X^{-3}-form for the energy. When we think of the property of interest as an energy-derivative concerning the Hamiltonian:

$$\hat{H}(\lambda) = \hat{H}(0) + \lambda\,\hat{V}, \tag{16}$$

then we can expand the correlation energy as:

$$E_{\mathrm{corr}}(\lambda, X) = \sum_{n=0}^{\infty}\sum_{k=0}^{\infty}\frac{C_n^{(k)}\lambda^k}{k!}X^{-n}. \tag{17}$$

The coefficients $C_n^{(0)}$ govern the convergence of the energy, the $C_n^{(1)}$ govern the convergence of the first-order property, and so on[53].

Let us finally have a brief look at the CBS (complete basis set) extrapolation to the MP2 limit developed by Petersson and co-workers[54−62], which is found in standard and widely distributed quantum chemistry programs. For pairs of occupied α and β spin-orbitals ($\alpha\beta$ pairs) and for $\alpha\alpha$-type second-order pair energies, the CBS extrapolation is based on the expressions:

$${}^{\alpha\beta}e_{ij}^{(2)}(N) = {}^{\alpha\beta}e_{ij}^{(2)}(\infty) + {}^{\alpha\beta}f_{ij}\frac{25}{512}(N + {}^{\alpha\beta}\delta_{ij})^{-1}, \tag{18}$$

$${}^{\alpha\alpha}e_{ij}^{(2)}(N) = {}^{\alpha\alpha}e_{ij}^{(2)}(\infty) + {}^{\alpha\alpha}f_{ij}\frac{25}{512}(N + {}^{\alpha\alpha}\delta_{ij})^{-5/3}, \tag{19}$$

where:

$${}^{\alpha\beta}f_{ij} = |S|_{ij}^2, \qquad {}^{\alpha\alpha}f_{ij} = 2|S|_{ij}^2\left(\frac{1-|S|_{ij}^2}{1+|S|_{ij}^2}\right), \tag{20}$$

and:

$$|S|_{ij} = \int |\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})|d\tau. \tag{21}$$

Equation (18) shows the same N^{-1}-dependence as found in (4), corresponding to the X^{-3}-form. This is the correct basis-set error of the principal expansion of the

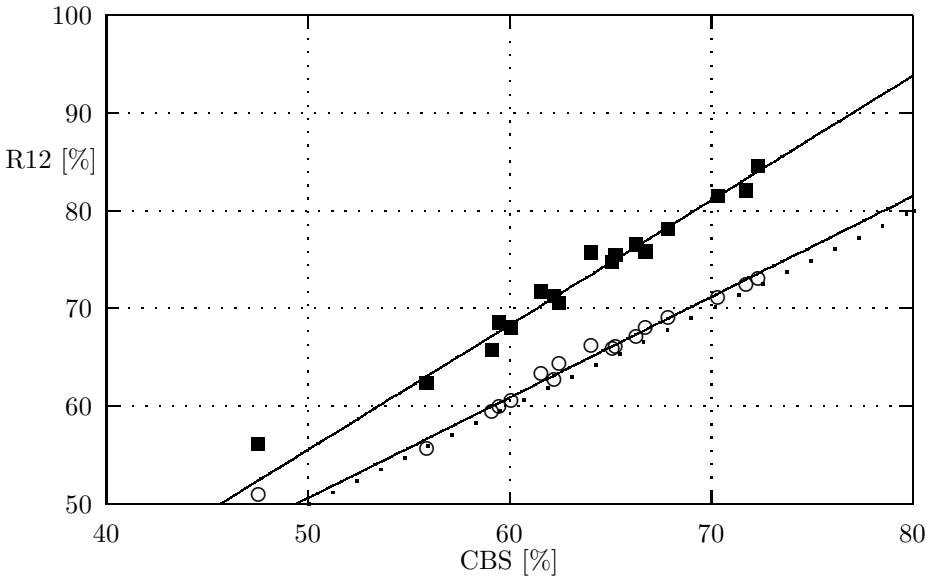

Figure 2. Ratio of CCSD(T) to MP2 basis-set errors, $\delta E_{\mathrm{CCSD(T)}}/\delta E_{\mathrm{MP2}}$, of the APNO basis set. Comparison of the ratio (i.e., interference factor) computed by the CBS-QCI/APNO method with the ratio obtained from R12 calculations. At the R12 level, the CCSD(T) error is $\delta E_{\mathrm{CCSD(T)}}$ = CCSD(T)-R12/B − CCSD(T)/APNO, while the MP2 error is either δE_{MP2} = MP2-R12/A − MP2/APNO (○) or δE_{MP2} = MP2-R12/B − MP2/APNO (■). The dotted line is a straight line with slope one through the origin.

He ground state. For a triplet state of He, however, or in general for triplet pair energies, the basis-set error of the principal expansion is X^{-5} (or $(L+1)^{-5}$).[32] This triplet basis-set error is reflected by the $(N + {}^{\alpha\alpha}\delta_{ij})^{-5/3}$ dependence.

We note that the $\alpha\beta$ and $\alpha\alpha$ pairs of the spin-orbital CBS method do not represent spin-adapted singlet and triplet pairs. Rather, the $\alpha\beta$ pair contributes to both singlet and triplet pairs. The purpose of the prefactors ${}^{\alpha\beta}f_{ij}$ and ${}^{\alpha\alpha}f_{ij}$ is to damp the extrapolated truncation errors for spatially distant pairs of (localized) orbitals.

In (18) and (19), ${}^{\alpha\beta}e_{ij}^{(2)}(\infty)$ and ${}^{\alpha\beta}\delta_{ij}$, which constitute the fitting parameters, are obtained from two-point fits. The first point is chosen as $N = 1$ – that is, as the Hartree–Fock calculation, for which ${}^{\alpha\beta}e_{ij}^{(2)}(1)$=0. A prescribed range of N values are then tried for the second point, each time computing the corresponding pair energy ${}^{\alpha\beta}e_{ij}^{(2)}(N)$. For each N, the two equations are solved for the two unknowns and the most negative ${}^{\alpha\beta}e_{ij}^{(2)}(\infty)$ is taken as the final, extrapolated second-order pair energy. The same procedure is followed for the $\alpha\alpha$ pairs.

To obtain the infinite-order corrections, the second-order corrections are scaled

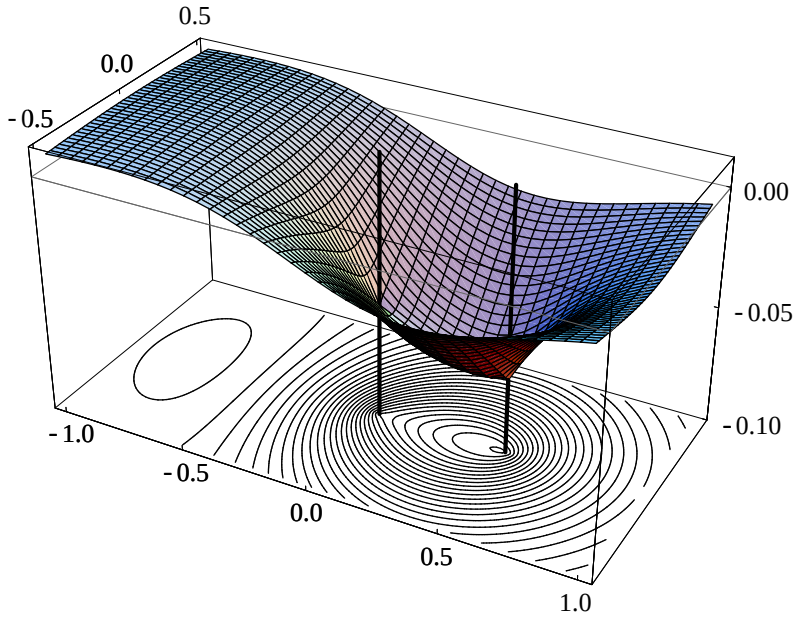

Figure 3. Coulomb hole (difference between the exact and the Hartree-Fock wavefunctions) of the He ground state as a function of the x_2 and y_2 coordinates of the second electron. The nucleus is located in the origin and the first electron is kept fixed at $x_1 = 0.5\ a_0$, $y_1 = z_1 = 0$.

by the interference factors:

$$\delta e_{ij}^{(\infty)} = \left(\sum_{\mu_{ij}=1}^{N_{\mathrm{virt}}+1} c_{\mu_{ij}}^{(1)} \right)^2 \delta e_{ij}^{(2)}, \tag{22}$$

computed from the first-order wavefunction. The scaling with this interference factor is remarkably accurate. For a variety of small closed-shell molecules[63], Figure 2 shows the overall CBS scaling factor – that is, the scaling factor for the sum of all pair energies – in comparison with the CCSD(T) to MP2 ratio as computed by the R12/A and R12/B methods. Hence, the interference factor appears to provide, by simple scaling, a reasonable estimate of the basis-set error at the CCSD(T) level once the corresponding MP2 basis-set error is known or obtained by extrapolation[62].

4 Coulomb hole

An explicit dependence of the wavefunction on r_{12} was already discussed by Slater[1] and Hylleraas[2] in the early days of quantum mechanics[64]. Slater and Hylleraas were concerned with the He atom, where the ground-state wavefunction can be written as a function $\Psi(r_1, r_2, r_{12})$ of the two nucleus-electron distances r_1 and r_2 and the electron-electron distance r_{12}. Then, the corresponding effective Schrödinger

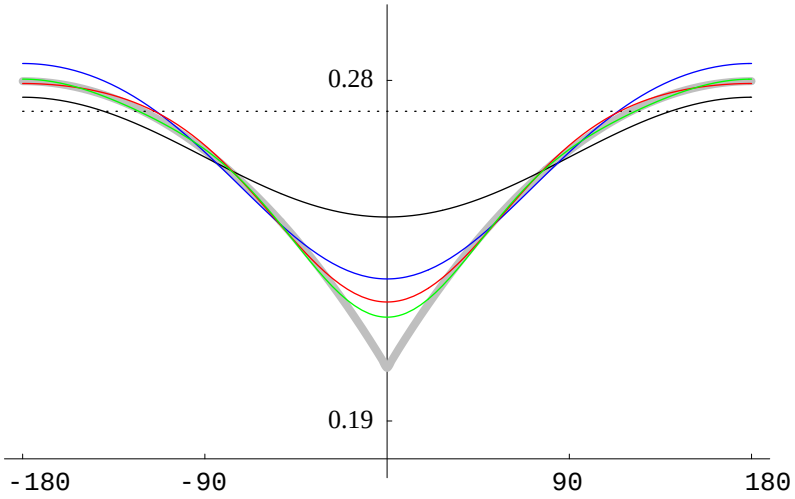

Figure 4. Coulomb hole of the He ground state. Comparison of standard CI wavefunctions obtained with the cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets (upper curves, from top to bottom) with the exact wavefunction $\Psi(r_1, r_2, r_{12})$ (lower curve) as a function of the angle θ_{12} (deg) between the position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, with fixed $r_1 = r_2 = 0.5\ a_0$.

equation has the form[2]:

$$H\,\Psi(r_1, r_2, r_{12}) = E\,\Psi(r_1, r_2, r_{12}), \tag{23}$$

with

$$\begin{aligned} H = &-\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{Z}{r_1} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{Z}{r_2} - \\ &- \frac{\partial^2}{\partial r_1 \partial r_{12}}\frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} - \frac{\partial^2}{\partial r_2 \partial r_{12}}\frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} - \\ &- \frac{\partial^2}{\partial r_{12}^2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{1}{r_{12}}, \end{aligned} \tag{24}$$

where Z is the nuclear charge. The exact solution to this equation should contain terms that balance the Coulomb singularities. For example, it should be ensured that:

$$\left\{ H\,\Psi(r_1, r_2, r_{12}) \right\}_{\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}_c} = E\,\Psi(r_c, r_c, 0) \tag{25}$$

for any point $\mathbf{r}_c$. This balance is established if:

$$\left\{ \frac{\partial \Psi(r_1, r_2, r_{12})}{\partial r_{12}} \right\}_{\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}_c} = \frac{1}{2}\Psi(r_c, r_c, 0), \tag{26}$$

because then the last and second-last terms of (24) cancel. Similar conditions can be derived for the Z/r_1 and Z/r_2 singularities. Equation (26) is known as Kato's

Table 5. Principal expansion of the two-electron Darwin energy (in $\mu E_{\rm h}$) of the He ground state[a,b].

$X=2$	$X=3$	$X=4$	$X=5$	$X=6$	$X=7$	$X=8$
-23.579	-21.564	-20.605	-20.039	-19.664	-19.397	-19.197

a As a function of numerically optimized cc-pVXZ basis sets[53].

b The exact value is $-\frac{\pi}{c^2}\langle\delta(r_{12})\rangle = -17.791\ \mu E_{\rm h}$.

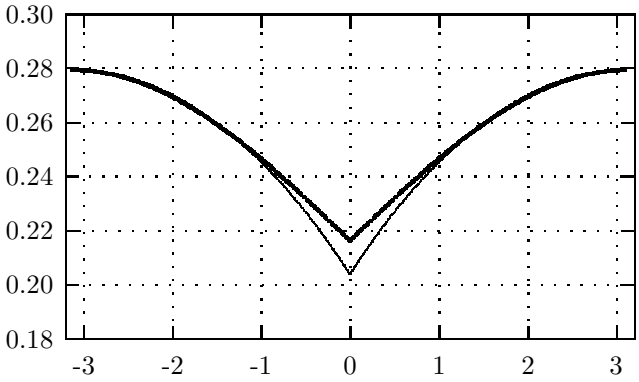

Figure 5. Coulomb hole of the He ground state. Comparison of the three-parameter Hylleraas function (33) (upper curve) with the exact wavefunction $\Psi(r_1, r_2, r_{12})$ (lower curve) as a function of the angle θ_{12} (rad) between the position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, with fixed $r_1 = r_2 = 0.5\ a_0$.

electron-electron cusp condition[65], which implies that for small r_{12} the (unnormalized) wavefunction behaves as:

$$\Psi(r_1, r_2, r_{12}) = 1 + \frac{1}{2} r_{12} + \mathcal{O}(r_{12}^2). \tag{27}$$

The cusp is easy to see at the bottom of the Coulomb hole in Figure 3.

A CI expansion in orbital products cannot reproduce this electron-electron cusp, as can be seen in Figure 4. At the bottom of the Coulomb hole of standard CI wavefunctions, there is no cusp as the first derivative is zero. Moreover, the convergence to the exact bottom of the Coulomb hole is extremely slow, as illustrated by the convergence of the expectation value $\langle\delta(r_{12})\rangle$, which is nothing but an integral over configuration space of the bottom of the Coulomb hole. This expectation value is related to the relativistic two-electron Darwin energy as:

$$E_{\text{two-electron Darwin}} = -\frac{\pi}{c^2}\langle\delta(r_{12})\rangle, \tag{28}$$

and this two-electron Darwin energy is displayed in Table 5 as a function of the cardinal number of numerically optimized cc-pVXZ basis sets. Interestingly, the two-electron Darwin term appears to converge as X^{-1}.[53] Thus, whereas the Coulomb hole itself converges as X^{-1}, its consequence for the correlation energy is that the latter converges as X^{-3}.

Hylleraas proposed to expand the He ground-state wavefunction as:

$$\Psi_N = \exp(-\zeta s) \sum_{i=1}^{N} c_i s^{l_i} t^{2m_i} u^{n_i}, \tag{29}$$

with:

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}. \tag{30}$$

The first function studied by Hylleraas was the 3-term function:

$$\Psi_3 = \exp(-\zeta s)(c_1 + c_2 u + c_3 t^2), \tag{31}$$

and the variationally determined energy for this function was $E = -2.902\,43\ E_\mathrm{h}$ for $\zeta = 1.816$. Hylleraas furthermore reported that he had spent considerable effort to find the next most important terms in the expansion (29). He ended up with the 6-term function:

$$\Psi_6 = \exp(-\zeta s)(c_1 + c_2 u + c_3 t^2 + c_4 s + c_5 s^2 + c_6 u^2), \tag{32}$$

leading to the energy $E = -2.903\,33\ E_\mathrm{h}$ for $\zeta = 1.756$.

It is truly amazing how accurate these compact wavefunctions are. Let us for example consider the 3-term function in more detail:

$$\Psi_3(r_1, r_2, r_{12}) = 1.331\, e^{-1.816(r_1+r_2)} \left[1 + 0.292\, r_{12} + 0.131\, (r_1 - r_2)^2\right]. \tag{33}$$

When we plot this wavefunction as a function of the angle between the position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, keeping the electrons fixed at a distance of $0.5\ a_0$ from the nucleus, we see that it already closely resembles the exact wavefunction (cf. Figure 5). In this plot, as r_1 and r_2 are constant, the function takes the form:

$$\Psi_3(0.5, 0.5, r_{12}) = 0.2165\, (1 + 0.292\, r_{12}), \tag{34}$$

that is, it has only one term linear in r_{12}. When comparing it with the standard CI wavefunctions in Figure 4, one is tempted to conclude that the 3-term Hylleraas-function is of an accuracy comparable to that of a cc-pVQZ- or cc-pV5Z/CI wavefunction. Indeed, the two-electron Darwin energy computed from the 3-term wavefunction amounts to $-19.427\ \mu E_\mathrm{h}$. This value is practically identical to the CI value ($-19.397\ \mu E_\mathrm{h}$) obtained with the fully optimized cc-pV7Z basis set! The correlation contribution from the 6-term Hylleraas-function is $-18.732\ \mu E_\mathrm{h}$. We can represent the two-electron Darwin energy as:

$$E_{\text{two-electron Darwin}}(X)/\mu E_\mathrm{h} = -17.791 - 11.25/X, \tag{35}$$

and thus, this 6-term value corresponds roughly to the $X = 12$ level.

5 Many-electron systems

For two-electron systems, the inclusion of r_{12} into the electronic wavefunction is not too difficult. The situation is different for many-electron systems, however. Hylleraas coordinates have been used in calculations on atoms with up to four electrons[66,67], but it is almost impossible to perform any useful calculations with

these coordinates on molecules with more than two electrons. This is very unfortunate because the Hylleraas expansion is in principle very rapidly convergent.

The very difficult many-electron many-center integrals are the reason why many-electron molecular calculations with Hylleraas coordinates are too complicated to be practical. In the remaining part of the present lecture, we will be concerned with the auxiliary techniques that are utilized to avoid the very difficult many-electron many-center integrals, thereby providing new opportunities for accurate calculations of molecular electronic structure.

6 Second quantization

We use the following notation for one- and many-electron functions:

$$\begin{aligned} \Psi,\ \Psi_N,\ \ldots &\quad n\text{-electron wavefunctions,} \\ \Phi,\ \Phi_k,\ |\Phi\rangle,\ |\Phi_i^a\rangle,\ |\Phi_{ij}^{ab}\rangle\ \ldots &\quad \text{Slater determinants,} \\ \varphi_\kappa,\ \varphi_p\ \ldots &\quad \text{orthonormal spin-orbitals,} \\ \chi_q\ \ldots &\quad \text{atomic basis functions.} \end{aligned}$$

Two-electron Slater determinants are also written as:

$$|ij\rangle = \frac{1}{\sqrt{2}}\big\{\varphi_i(1)\varphi_j(2) - \varphi_i(2)\varphi_j(1)\big\}. \tag{36}$$

We employ a given, finite basis set $\{\varphi_p\}$ of one-electron functions in which the calculations are performed as well as a complete set $\{\varphi_\kappa\}$, which is used in the second-quantization formalism. Orbital indices are used as follows:

$$\begin{aligned} i,\ j,\ k,\ \ldots &\quad \text{occupied spin-orbitals,} \\ a,\ b,\ c,\ \ldots &\quad \text{virtual spin-orbitals within the given basis set,} \\ p,\ q,\ r,\ \ldots &\quad \text{arbitrary spin-orbitals within the given basis set,} \\ \alpha,\ \beta,\ \gamma,\ \ldots &\quad \text{virtual spin-orbitals within a complete basis set,} \\ \kappa,\ \lambda,\ \mu,\ \ldots &\quad \text{arbitrary spin-orbitals that form a complete basis set.} \end{aligned}$$

This convention is illustrated in Figure 6. Antisymmetrized integrals and replacement operator amplitudes are written in tensor form[68−70]:

$$X_p^q = \langle p|X|q\rangle, \quad \bar{Y}_{rs}^{pq} = \langle rs|Y|pq\rangle, \tag{37}$$

assuming the Einstein summation convention over repeated indices. In the second-quantization particle-hole formalism, the closed-shell reference state $|\Phi\rangle$ is taken as the physical vacuum and the Hamiltonian is shifted by the reference energy. With $g = r_{12}^{-1}$ and h the usual one-electron Hamiltonian, the normal-ordered Hamiltonian can be written as:

$$H_N = H - \langle\Phi|H|\Phi\rangle = F_N + W_N, \tag{38}$$

$$F_N = f_\kappa^\lambda \tilde{a}_\lambda^\kappa, \quad f_\kappa^\lambda = h_\kappa^\lambda + \bar{g}_{\kappa i}^{\lambda i}, \quad W_N = \tfrac{1}{4}\bar{g}_{\kappa\lambda}^{\mu\nu}\tilde{a}_{\mu\nu}^{\kappa\lambda}, \tag{39}$$

in terms of the orthonormal one-electron basis $\{\varphi_\kappa\}$. Greek letters emphasize that the second-quantized Hamiltonian is exact only if it is defined in terms of a complete

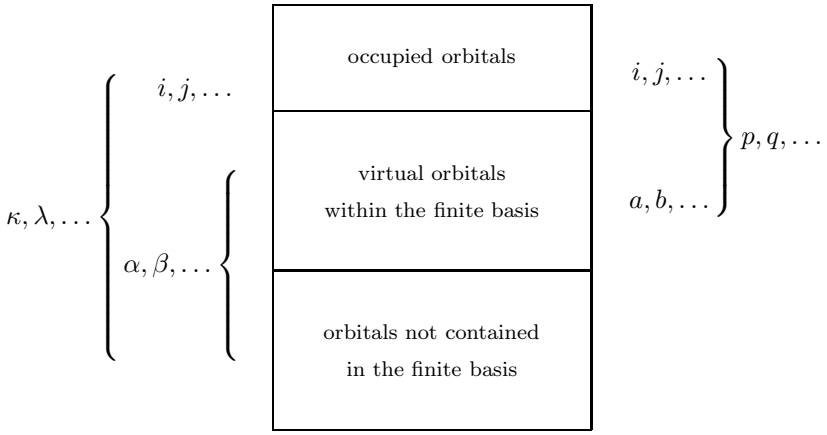

Figure 6. Illustration of the spaces spanned by the one-particle basis functions: $i, j, \cdots$ = occupied spin-orbitals, $a, b, \cdots$ = non-occupied spin-orbitals contained in the finite basis, $\alpha, \beta, \cdots$ = complete set of virtuals, $p, q, \cdots$ = arbitrary spin-orbital contained in the finite basis, $\kappa, \lambda, \cdots$ = complete basis set.

basis set. The $\tilde{a}^{\kappa}_{\lambda}$ and $\tilde{a}^{\kappa\lambda}_{\nu\mu}$ are replacement operators in normal order, defined with respect to $|\Phi\rangle$ according to:

$$\tilde{a}^{q_1 q_2 \ldots q_n}_{p_1 p_2 \ldots p_n} = (\tilde{a}^{p_1 p_2 \ldots p_n}_{q_1 q_2 \ldots q_n})^{\dagger} = \{a^{\dagger}_{q_1} a^{\dagger}_{q_2} \ldots a^{\dagger}_{q_n} a_{p_n} \ldots a_{p_2} a_{p_1}\}, \tag{40}$$

where $a^{\dagger}_{q}$ and a_p are creation and annihilation operators, respectively. The braces in (40) denote the normal-ordering with respect to the physical vacuum, while the counterparts of (40) without a tilde refer to the genuine vacuum. The multiplicative first-quantized operator $r = \sum_{i<j} r_{ij}$ of the interelectronic coordinates can thus be written in the second-quantization form:

$$r = \tfrac{1}{4} \bar{r}^{\mu\nu}_{\kappa\lambda} a^{\kappa\lambda}_{\mu\nu}. \tag{41}$$

If $|\Phi\rangle$ is the Hartree-Fock reference, the f^{λ}_{κ}'s in (39) are elements of the Fock matrix. In terms of canonical orbitals this matrix is diagonal – that is, $f^{\lambda}_{\kappa} = \delta^{\lambda}_{\kappa} \varepsilon_{\lambda}$.

7 Explicitly correlated coupled-cluster doubles model

In single-reference coupled-cluster doubles (CCD) theory, the wavefunction is written in the exponential form:

$$|\Psi\rangle = e^{S} |\Phi\rangle, \tag{42}$$

where $|\Phi\rangle$ is the Hartree-Fock determinant and S the cluster operator, which in this special case is restricted to all double replacements:

$$S \equiv T_2 = \tfrac{1}{4} t^{ij}_{ab} a^{ab}_{ij}. \tag{43}$$

The energy and the amplitudes are determined by:

$$E = \langle \Phi | \tilde{H}_S | \Phi \rangle, \quad \tilde{H}_S = e^{-S} H e^{S}, \tag{44}$$

$$\langle\left(\frac{\partial S\Phi}{\partial t_{ab}^{ij}}\right)|\tilde{H}_S|\Phi\rangle = 0. \tag{45}$$

Jeziorski *et al.*[71] have formulated a first-quantization form of the CCD equations where the pair functions are not expressed in terms of double replacements – as in the orbital approximation – but as expansions in Gaussian geminals. In the original derivation of the theory, they have employed a spin-adapted formulation in terms of singlet and triplet pairs but we will discuss the theory in a spin-orbital formalism.

In the first-quantization formulation, the cluster operator is written as a sum of two-electron operators:

$$T_2 = \sum_{\mu\langle\nu} t(\mu\nu), \quad t(12) = \sum_{i\langle j} |\tau_{ij}\rangle\langle ij|. \tag{46}$$

For each pair of occupied spin-orbitals there is one pair function $|\tau_{ij}\rangle$, which is determined by solving the coupled CCD equations for all pairs simultaneously. In conventional CCD theory, that is, in the orbital approximation, each $|\tau_{ij}\rangle$ is expanded as:

$$|\tau_{ij}\rangle = \sum_{a\langle b} t_{ab}^{ij} |ab\rangle, \tag{47}$$

but Szalewicz *et al.*[72–85] expand the pair function in a basis of (Gaussian) geminals:

$$|\tau_{ij}\rangle = \sum_{k_{ij}} c_{k_{ij}}\, Q_{\rm occ}(12)\, \mathcal{A}\big\{\Theta_{k_{ij}}(12)\, G_{k_{ij}}(12)\big\}. \tag{48}$$

The notation with k_{ij} indicates that both the expansion length and the geminals themselves can be chosen individually for each pair of occupied orbitals. $\Theta_{k_{ij}}(12)$ is a proper spin function and the projection operator:

$$Q_{\rm occ}(12) = \big\{1 - P_{\rm occ}(1)\big\}\big\{1 - P_{\rm occ}(2)\big\}, \quad P_{\rm occ} = \sum_i |\varphi_i\rangle\langle\varphi_i| \tag{49}$$

ensures that the $|\tau_{ij}\rangle$'s satisfy the strong-orthogonality condition:

$$|\tau_{ij}\rangle = Q_{\rm occ}(12)\, |\tau_{ij}\rangle. \tag{50}$$

Obviously, the amplitudes are obtained from:

$$\langle\left(\frac{\partial S\Phi}{\partial c_{k_{ij}}}\right)|\tilde{H}_S|\Phi\rangle = 0. \tag{51}$$

A second-quantization formulation can be used if a complete basis set is introduced formally (cf. Section 6). This is convenient for the discussion of the various many-electron integrals that appear when geminals are employed in the framework of CCD theory. In particular, up to four-electron integrals occur in the MP2, MP3, LCCD (linearized coupled-cluster doubles), and FCCD (factorizable coupled-cluster doubles) approaches. The complete CCD equations involve five-electron integrals and the FCCD approximation to CCD consists of ignoring the (nonfactorizable) terms or diagrams that involve these five-electron integrals.

Using the complete basis set notation, the cluster operator can be written as:

$$T_2 = \tfrac{1}{4} c_{k_{ij}}^{ij} \bar{G}_{\alpha\beta}^{k_{ij}} a_{ij}^{\alpha\beta}, \quad c_{k_{ij}}^{ij} \equiv c_{k_{ij}} \tag{52}$$

where:

$$\bar{G}_{\alpha\beta}^{k_{ij}} = \langle \alpha\beta | \mathcal{A}\big\{ \Theta_{k_{ij}}(12)\, G_{k_{ij}}(12) \big\} \rangle. \tag{53}$$

$\bar{G}_{\alpha\beta}^{k_{ij}}$ is the two-electron overlap between two virtual orbitals and a geminal. Note that the projection operator $Q_{\mathrm{occ}}(12)$ is not needed in (53) by virtue of $\langle \alpha\beta |$. The CCD energy and amplitude equations can be written schematically as[86]:

$$E = \tfrac{1}{2} A_{ij}^{k_{ij}} c_{k_{ij}}^{ij}, \tag{54}$$

$$A_{k_{ij}}^{ij} + (L_1)_{k_{ij}}^{ij} + (L_2)_{k_{ij}}^{ij} + Q_{k_{ij}}^{ij} = 0, \tag{55}$$

where A, L, and Q represent the absolute, linear, and quadratic terms, respectively. The absolute term takes the following form:

$$A_{k_{ij}}^{ij} = \langle \left(\frac{\partial S\Phi}{\partial c_{k_{ij}}^{ij}} \right) | W_N | \Phi \rangle = \tfrac{1}{2} \bar{G}_{k_{ij}}^{\alpha\beta} \bar{g}_{\alpha\beta}^{ij} = \langle \mathcal{A}\big\{ \Theta_{k_{ij}}(12)\, G_{k_{ij}}(12) \big\} | Q_{\mathrm{occ}}(12) \frac{1}{r_{12}} | ij \rangle. \tag{56}$$

This term contains three-electron integrals due to the strong-orthogonality projector $Q_{\mathrm{occ}}(12)$, for example:

$$\langle G_{k_{ij}}(12) || \varphi_m(1) \rangle \langle \varphi_m(1) | \frac{1}{r_{12}} | \varphi_i(1) \varphi_j(2) \rangle = \langle G_{k_{ij}}(12) \varphi_m(3) | \frac{1}{r_{32}} | \varphi_m(1) \varphi_j(2) \varphi_i(3) \rangle. \tag{57}$$

Using the two-index antisymmetrizer $\mathcal{A}_{ij} = 1 - (i \leftrightarrow j)$, the first of the two linear terms is:

$$\begin{aligned} (L_1)_{k_{ij}}^{ij} &= \langle \left(\frac{\partial S\Phi}{\partial c_{k_{ij}}^{ij}} \right) | [F_N, S] | \Phi \rangle \\ &= \tfrac{1}{2} \bar{G}_{k_{ij}}^{\alpha\beta} \Big(\mathcal{A}_{\alpha\beta} f_\alpha^\gamma \bar{G}_{\gamma\beta}^{l_{ij}} c_{l_{ij}}^{ij} - \mathcal{A}_{ij} f_k^i \bar{G}_{\alpha\beta}^{l_{kj}} c_{l_{kj}}^{kj} \Big). \end{aligned} \tag{58}$$

The term involving the f_k^i elements of the Fock matrix is related to the overlap matrix of the geminals and involves three-electron integrals. The other term, however, is more complicated. After realizing that $f_\alpha^\gamma = h_\alpha^\gamma + \bar{g}_{\alpha i}^{\gamma i}$ it becomes clear that it contains four-electron integrals. Note that this term also occurs in MP2 theory. The second linear term is:

$$\begin{aligned} (L_2)_{k_{ij}}^{ij} &= \langle \left(\frac{\partial S\Phi}{\partial c_{k_{ij}}^{ij}} \right) | [W_N, S] | \Phi \rangle \\ &= \tfrac{1}{2} \bar{G}_{k_{ij}}^{\alpha\beta} \Big(\tfrac{1}{2} \bar{g}_{\alpha\beta}^{\gamma\delta} \bar{G}_{\gamma\delta}^{l_{ij}} c_{l_{ij}}^{ij} + \tfrac{1}{2} \bar{g}_{kl}^{ij} \bar{G}_{\alpha\beta}^{l_{kl}} c_{l_{kl}}^{kl} + \mathcal{A}_{\alpha\beta} \mathcal{A}_{ij} \bar{g}_{\alpha k}^{i\gamma} \bar{G}_{\beta\gamma}^{l_{jk}} c_{l_{jk}}^{jk} \Big). \end{aligned} \tag{59}$$

The three distinct terms (or diagrams) contain four-electron, three-electron, and four-electron integrals, in the order of appearance. Finally, the quadratic term is:

$$\begin{aligned} Q^{ij}_{k_{ij}} &= \tfrac{1}{2}\langle\left(\frac{\partial S\Phi}{\partial c^{ij}_{k_{ij}}}\right)|[[W_N,S],S]|\Phi\rangle \\ &= \tfrac{1}{2}\bar{G}^{\alpha\beta}_{k_{ij}}\Big(\mathcal{A}_{\alpha\beta}\bar{G}^{l_{ik}}_{\alpha\gamma}c^{ik}_{l_{ik}}\bar{G}^{l_{jl}}_{\beta\delta}c^{jl}_{l_{jl}} + \tfrac{1}{2}\mathcal{A}_{\alpha\beta}\bar{G}^{l_{ij}}_{\alpha\delta}c^{ij}_{l_{ij}}\bar{G}^{l_{kl}}_{\beta\gamma}c^{kl}_{l_{kl}} \\ &+ \tfrac{1}{2}\mathcal{A}_{ij}\bar{G}^{l_{il}}_{\alpha\beta}c^{il}_{l_{il}}\bar{G}^{l_{jk}}_{\gamma\delta}c^{jk}_{l_{jk}} + \tfrac{1}{4}\bar{G}^{l_{ij}}_{\gamma\delta}c^{ij}_{l_{ij}}\bar{G}^{l_{kl}}_{\alpha\beta}c^{kl}_{l_{kl}}\Big)\bar{g}^{\gamma\delta}_{kl}. \end{aligned} \tag{60}$$

The last two terms in (60) factorize into products of three-electron integrals, but the first two terms involve five-electron integrals. However, these terms are ignored in the FCCD approximation (the whole quadratic term is, of course, absent in the LCCD approach). For not too large systems, it is believed that this nonfactorizable term is small and can be neglected.

Clearly, the computation of four- and five-electron integrals is a serious obstacle for large-scale applications on molecules of the geminals-based CCD approach.

Szalewicz and co-workers[72−75] have developed alternative approaches that involve only three-electron integrals at the MP2, MP3, LCCD, and FCCD levels (and four-electron integrals at the complete CCD level) by introducing new computational techniques. The techniques have been designated as weak orthogonality (WO), super weak orthogonality (SWO), and SWO plus projection (SWOP), and the techniques are sketched in the following section.

8 Weak orthogonality techniques

In order to illustrate the simplifications introduced by Szalewicz *et al.*[72−75] it is convenient to define an iterative CCD procedure by rewriting (55) as:

$$-(L_1)^{ij}_{k_{ij}} = A^{ij}_{k_{ij}} + (L_2)^{ij}_{k_{ij}} + Q^{ij}_{k_{ij}} \equiv \tfrac{1}{2}\bar{G}^{\alpha\beta}_{k_{ij}}V^{ij}_{\alpha\beta} \tag{61}$$

The meaning of V is easily recognized in (56), (59), and (60). Using canonical Hartree-Fock orbitals, the iterative process takes the form:

$$-\tfrac{1}{2}\bar{G}^{\alpha\beta}_{k_{ij}}\left(f^{\gamma}_{\alpha}\bar{G}^{l_{ij}}_{\gamma\beta} + f^{\gamma}_{\beta}\bar{G}^{l_{ij}}_{\alpha\gamma} - (\varepsilon_i+\varepsilon_j)\bar{G}^{l_{ij}}_{\alpha\beta}\right)c^{ij\ [n+1]}_{l_{ij}} = \tfrac{1}{2}\bar{G}^{\alpha\beta}_{k_{ij}}V^{ij}_{\alpha\beta}(\mathbf{c}^{[n]}). \tag{62}$$

The first simplification (WO) is achieved by replacing the l.h.s of (62) by an analogous expression without strong-orthogonality projector, that is[72]:

$$-\tfrac{1}{2}\bar{G}^{\kappa\lambda}_{k_{ij}}\left(\tilde{f}^{\mu}_{\kappa}\bar{G}^{l_{ij}}_{\mu\lambda} + \tilde{f}^{\mu}_{\lambda}\bar{G}^{l_{ij}}_{\kappa\mu} - (\varepsilon_i+\varepsilon_j)\bar{G}^{l_{ij}}_{\kappa\lambda}\right)c^{ij\ [n+1]}_{l_{ij}} = \tfrac{1}{2}\bar{G}^{\alpha\beta}_{k_{ij}}V^{ij}_{\alpha\beta}(\mathbf{c}^{[n]}), \tag{63}$$

which eliminates the four-electron integrals in L_1. The operator $\tilde{f}$ is defined as:

$$\tilde{f}(1) = f(1) + \Delta_{ij}P_{\mathrm{occ}}(1), \tag{64}$$

with:

$$\Delta_{ij} = \tfrac{1}{2}(\varepsilon_i+\varepsilon_j) - \varepsilon_{\min} + \eta, \tag{65}$$

where $\varepsilon_{\min}$ is the lowest eigenvalue and η a positive parameter (note that the operator $\tilde{f}(1)$ depends on the electron pair ij). Some improved WO functionals are proposed and described in the more recent literature[76,82]. The second approximation (SWO) is concerned with the r.h.s. of 62, which is replaced by:

$$-\tfrac{1}{2}\bar{G}^{\kappa\lambda}_{k_{ij}}\left(\tilde{f}^{\mu}_{\kappa}\bar{G}^{l_{ij}}_{\mu\lambda}+\tilde{f}^{\mu}_{\lambda}\bar{G}^{l_{ij}}_{\kappa\mu}-(\varepsilon_i+\varepsilon_j)\bar{G}^{l_{ij}}_{\kappa\lambda}\right)c^{ij\ [n+1]}_{l_{ij}}$$
$$=\tfrac{1}{2}\left(\bar{G}^{\kappa\lambda}_{k_{ij}}V^{ij}_{\kappa\lambda}(\mathbf{c}^{[n]})-\bar{G}^{mn}_{k_{ij}}V^{ij}_{mn}(\mathbf{c}^{[n]})\right). \tag{66}$$

The third simplification (SWOP) consists of re-expanding after each CCD iteration the strongly orthogonalized pair functions in the corresponding basis of geminals by solving the set of linear equations[75]:

$$\bar{G}^{\kappa\lambda}_{m_{ij}}\bar{G}^{k_{ij}}_{\kappa\lambda}\,\tilde{c}^{ij\ [n]}_{k_{ij}}=G^{\alpha\beta}_{m_{ij}}\bar{G}^{l_{ij}}_{\alpha\beta}\,c^{ij\ [n]}_{l_{ij}}. \tag{67}$$

The amplitudes $\tilde{\mathbf{c}}^{[n]}$ are inserted into a modified iterative process:

$$-\tfrac{1}{2}\bar{G}^{\kappa\lambda}_{k_{ij}}\left(\tilde{f}^{\mu}_{\kappa}\bar{G}^{l_{ij}}_{\mu\lambda}+\tilde{f}^{\mu}_{\lambda}\bar{G}^{l_{ij}}_{\kappa\mu}-(\varepsilon_i+\varepsilon_j)\bar{G}^{l_{ij}}_{\kappa\lambda}\right)c^{ij\ [n+1]}_{l_{ij}}$$
$$=\tfrac{1}{2}\left(\bar{G}^{\kappa\lambda}_{k_{ij}}\tilde{V}^{ij}_{\kappa\lambda}(\tilde{\mathbf{c}}^{[n]})-\bar{G}^{mn}_{k_{ij}}\tilde{V}^{ij}_{mn}(\tilde{\mathbf{c}}^{[n]})\right). \tag{68}$$

Note that this equation contains $\tilde{V}$, which is analogous to V but with the strong-orthogonality projectors removed. In the second-quantization notation, this means that in $\tilde{V}$ all $\alpha,\beta,\ldots$ appearing in V are replaced by the indices $\kappa,\lambda,\ldots$ of the entire basis. New amplitudes $\mathbf{c}^{[n+1]}$ are obtained and subsequently re-expanded according to (67).

The SWOP-FCCD approach is an approximative CCD method that is drastically less demanding than the corresponding rigorous and complete treatment. To illustrate this, let the one-particle basis set has dimension M and the geminal basis dimension K (i.e., the same dimension for all pairs). By inspection of (60) it becomes clear that the complete CCD approach would require the computation of M^4K^3 five-electron integrals. The FCCD method would require M^4K^2 four-electron integrals in L_1 and L_2 if no weak orthogonality techniques were introduced and only M^2K^2 (and M^4K) three-electron integrals in the SWOP framework. Hence, MP2 calculations based on the WO functional involve $aM^2K^2+bM^4K$ three-electron integrals and so do the LCCD and FCCD methods based on the SWOP technique. A SWOP-FCCD computation is not substantially more time consuming than a third-order calculation.

The most elaborate CCD – and partly CCSD – calculations with Gaussian geminals have been performed on small atomic and diatomic systems such as Be, LiH, and Ne[76]. Unfortunately, the geminals-based coupled-cluster approach has not yet evolved to a widely applicable tool of numerical quantum chemistry, and not many applications are known. Recently, however, second-order results for H_2O have been reported[82].

It is stressed that the WO, SWO, and SWOP techniques are not approximations. These are different methods to enforce the strong orthogonality, capable of giving

the exact results provided that the employed geminal basis set is sufficiently large. If we aim at extremely accurate results, then these techniques are certainly helpful tools, but their rôle is not clear when we plan to use geminals to compute efficiently the bulk of dynamical correlation (of the order of 90%).

For more details on the geminals-based CCSD method the reader is referred to the very recent ans comprehensive overview presented by Bukowski *et al.*[85]

9 R12 methods

The R12 methods have first been proposed by Kutzelnigg in 1985[87]. They have been implemented at various levels of many-body perturbation theory and at the coupled-cluster level[88−93]. A detailed description of the coupled-cluster theory with linear R12 terms has been presented by Noga and Kutzelnigg[94], and we will therefore focus only on the main formulae in the present section. It is also noted that Gdanitz[95,96] has extended the application of R12 methods to the multireference case.

The CCD-R12 ansatz is:

$$T_2 = \tfrac{1}{8} c_{kl}^{ij} \bar{R}_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta} + \tfrac{1}{4} t_{ab}^{ij} a_{ij}^{ab}, \tag{69}$$

with:

$$\bar{R}_{\mu\nu}^{kl} = \langle \mu\nu | Q(12)\, r_{12} \, |kl\rangle \;=\; \bar{r}_{\mu\nu}^{kl} - \delta_\nu^q \bar{r}_{\mu q}^{kl} - \delta_\mu^p \bar{r}_{p\nu}^{kl} + \tfrac{1}{2} \Delta_{\mu\nu}^{pq} \bar{r}_{pq}^{kl}, \tag{70}$$

where:

$$\Delta_{\kappa\lambda}^{\mu\nu} = \delta_\kappa^\mu \delta_\lambda^\nu - \delta_\lambda^\mu \delta_\kappa^\nu \tag{71}$$

and:

$$Q(12) = \{1 - P(1)\}\{1 - P(2)\}, \quad P = \sum_p |\varphi_p\rangle\langle\varphi_p|. \tag{72}$$

The use of the operator $\bar{R}$ implies that the r_{12}-dependent functions $\bar{R}_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta} |\Phi\rangle$ are strongly orthogonal to all Slater determinants built from orbitals contained in the finite basis set. This is very convenient. In a first-quantization form[97], the ansatz (69–70) is:

$$T_2 = \sum_{\mu\langle\nu} t(\mu\nu), \tag{73}$$

$$t(12) = \sum_{i\langle j} \sum_{k\langle l} c_{kl}^{ij}\, Q(12)\, r_{12}\, |kl\rangle\langle ij| + \sum_{i\langle j} \sum_{a\langle b} t_{ab}^{ij}\, |ab\rangle\langle ij|. \tag{74}$$

There are two coupled sets of amplitude equations, one for the conventional amplitudes t:

$$A_{ab}^{ij} + (L_1)_{ab}^{ij} + (L_2)_{ab}^{ij} + Q_{ab}^{ij} = 0, \tag{75}$$

and one for the r_{12}-dependent amplitudes c:

$$A_{kl}^{ij} + (L_1)_{kl}^{ij} + (L_2)_{kl}^{ij} + Q_{kl}^{ij} = 0, \tag{76}$$

while the energy is given by:

$$E = \tfrac{1}{4}(A_{ij}^{kl} c_{kl}^{ij} + A_{ij}^{ab} t_{ab}^{ij}). \tag{77}$$

Here and in the following, it is understood that the A, L_1, L_2, and Q terms refer to the amplitude equations determining the r_{12}-dependent amplitudes c if all four sub- and superscripts are indices of occupied orbitals and to the equations determining the conventional amplitudes t otherwise.

The absolute terms take the form:

$$A_{ab}^{ij} = \langle \left(\frac{\partial S\Phi}{\partial t_{ab}^{ij}} \right) | W_N | \Phi \rangle = \bar{g}_{ab}^{ij}, \tag{78}$$

$$A_{kl}^{ij} = \langle \left(\frac{\partial S\Phi}{\partial c_{kl}^{ij}} \right) | W_N | \Phi \rangle = \tfrac{1}{2} \bar{R}_{kl}^{\alpha\beta} \bar{g}_{\alpha\beta}^{ij}. \tag{79}$$

Application of the standard approximation[70] to (79) gives:

$$\tfrac{1}{2} \bar{R}_{kl}^{\alpha\beta} \bar{g}_{\alpha\beta}^{ij} = \tfrac{1}{2} \left(\bar{r}_{kl}^{\kappa\lambda} \bar{g}_{\kappa\lambda}^{ij} - \bar{r}_{kl}^{p\lambda} \bar{g}_{p\lambda}^{ij} - \bar{r}_{kl}^{\kappa q} \bar{g}_{\kappa q}^{ij} + \bar{r}_{kl}^{pq} \bar{g}_{pq}^{ij} \right) \approx \Delta_{kl}^{ij} - \tfrac{1}{2} \bar{r}_{kl}^{pq} \bar{g}_{pq}^{ij}, \tag{80}$$

which only involves two-electron integrals over the operators r_{12} and r_{12}^{-1}.

The L_1 terms are

$$(L_1)_{ab}^{ij} = \langle \left(\frac{\partial S\Phi}{\partial t_{ab}^{ij}} \right) | [F_N, S] | \Phi \rangle = \mathcal{A}_{ab} f_a^c t_{cb}^{ij} - \mathcal{A}_{ij} f_k^i t_{ab}^{kj}, \tag{81}$$

$$\begin{aligned} (L_1)_{kl}^{ij} &= \langle \left(\frac{\partial S\Phi}{\partial c_{kl}^{ij}} \right) | [F_N, S] | \Phi \rangle \\ &= \tfrac{1}{2} \bar{R}_{kl}^{\alpha\beta} \left(\mathcal{A}_{\alpha\beta} f_\alpha^\gamma \bar{R}_{\gamma\beta}^{mn} c_{mn}^{ij} - \mathcal{A}_{ij} f_o^i \bar{R}_{\alpha\beta}^{mn} c_{mn}^{oj} \right). \end{aligned} \tag{82}$$

There is no coupling between the conventional and r_{12}-dependent L_1 terms by virtue of the strongly orthogonal $\bar{R}$. Since MP2-R12 theory is obtained by removing the L_2 and Q terms from (75) and (76), this level of theory is exactly decoupled[98], that is, the MP2-R12 energy is a sum of the conventional MP2 energy and a contribution from the r_{12}-dependent terms. Therefore, this r_{12}-dependent contribution has been denoted in previous work as "basis set incompleteness correction", as it represents a contribution that is computed independently and added to the conventional MP2 energy. The latter is computed as usual in the prescribed basis.

A coupling between the conventional and r_{12}-dependent amplitudes appears for the first time in the L_2 terms:

$$(L_2)_{ab}^{ij} = \tfrac{1}{2} \bar{g}_{kl}^{ij} t_{ab}^{kl} + \tfrac{1}{2} \bar{g}_{ab}^{cd} t_{cd}^{ij} + \mathcal{A}_{ij} \mathcal{A}_{ab} \bar{g}_{ak}^{ic} t_{bc}^{jk} + \tfrac{1}{4} \bar{g}_{ab}^{\gamma\delta} \bar{R}_{\gamma\delta}^{kl} c_{kl}^{ij}. \tag{83}$$

Introducing the amplitude-free intermediate:

$$\bar{V}_{ab}^{kl} = \tfrac{1}{2} \bar{g}_{ab}^{\gamma\delta} \bar{R}_{\gamma\delta}^{kl} = \tfrac{1}{2} \bar{g}_{ab}^{\kappa\lambda} \bar{R}_{\kappa\lambda}^{kl} \approx -\tfrac{1}{2} g_{ab}^{pq} \bar{r}_{pq}^{kl}, \tag{84}$$

this term can be evaluated in a straightforward manner as:

$$(L_2)_{ab}^{ij} = \tfrac{1}{2} \bar{g}_{kl}^{ij} t_{ab}^{kl} + \tfrac{1}{2} \bar{g}_{ab}^{cd} t_{cd}^{ij} + \mathcal{A}_{ij} \mathcal{A}_{ab} \bar{g}_{ic}^{ak} t_{jk}^{bc} + \tfrac{1}{2} \bar{V}_{ab}^{kl} c_{kl}^{ij}. \tag{85}$$

In terms of the effective interactions $\bar{P}$, $\bar{X}$, and $\bar{Z}$, the r_{12}-dependent L_2 amplitude equation can be written as:

$$(L_2)^{ij}_{kl} = \tfrac{1}{2}\Big\{(\bar{V}^\dagger)^{ab}_{kl}t^{ij}_{ab} + \bar{P}^{oo'}_{kl}c^{ij}_{oo'} + \tfrac{1}{2}\bar{X}^{oo'}_{kl}\bar{c}^{mn}_{oo'}\bar{g}^{ij}_{mn} - \mathcal{A}_{ij}\bar{Z}^{oo';i}_{kl;m}c^{mj}_{oo'}\Big\}. \tag{86}$$

The $\bar{X}$ and $\bar{P}$ intermediates are easily computed in the standard approximation:

$$\bar{X}^{ij}_{kl} \approx \overline{(r^2)}^{ij}_{kl} - \tfrac{1}{2}\bar{r}^{pq}_{kl}\bar{r}^{ij}_{pq}, \quad P^{oo'}_{kl} \approx \tfrac{1}{4}\bar{r}^{rs}_{kl}\bar{g}^{pq}_{rs}\bar{r}^{oo'}_{pq} - \bar{r}^{oo'}_{kl}. \tag{87}$$

The effective interaction $\bar{Z}^{oo';i}_{kl;m}$ is, however, more complicated. Its evaluation has been discussed in detail by Noga and Kutzelnigg[94] in the Appendix F of their paper. Intermediates of the type $\bar{Z}^{kl;i}_{kl;m}$ already appeared in the early MP3, CID, and LCCD calculations based on the former, non-orbital-invariant ansatz[99]. In these calculations, the evaluation of the $\bar{Z}$ term was performed according this Appendix F[94]:

$$\begin{aligned}\bar{Z}^{kl;q}_{ij;p} &= \bar{R}^{\alpha\beta}_{ij}\bar{g}^{q\gamma}_{p\beta}\bar{R}^{kl}_{\alpha\gamma} \approx \bar{R}^{\alpha\beta}_{ij}g^{q\gamma}_{p\beta}\bar{R}^{kl}_{\alpha\gamma} = \bar{R}^{\mu\nu}_{ij}g^{q\lambda}_{p\nu}\bar{R}^{kl}_{\mu\lambda}\\ &\approx \bar{R}^{\mu\nu}_{ij}g^{q\lambda}_{p\nu}\bar{r}^{kl}_{\mu\lambda} + \bar{r}^{\mu\nu}_{ij}g^{q\lambda}_{p\nu}\bar{R}^{kl}_{\mu\lambda} - \bar{r}^{\mu\nu}_{ij}g^{q\lambda}_{p\nu}\bar{r}^{kl}_{\mu\lambda} + \bar{r}^{rs}_{ij}g^{qt}_{ps}\bar{r}^{kl}_{rt}\\ &\approx \mathcal{A}_{ij}g^{qr}_{pi}\bar{Y}^{kl}_{rj} + \mathcal{A}_{kl}g^{qk}_{pr}\bar{Y}^{rl}_{ij} + \bar{r}^{rs}_{ij}g^{qt}_{ps}\bar{r}^{kl}_{rt},\end{aligned} \tag{88}$$

where:

$$\bar{Y}^{rs}_{pq} = \bar{X}^{rs}_{pq} - \tfrac{1}{2}\overline{(r^2)}^{rs}_{pq}. \tag{89}$$

The quadratic term to the conventional doubles amplitude equation is:

$$\begin{aligned}Q^{ij}_{ab} = &\Big[\mathcal{A}_{ab}(t^{ik}_{ac}t^{jl}_{bd} + \tfrac{1}{2}t^{ij}_{ad}t^{kl}_{bc}) + \tfrac{1}{2}\mathcal{A}_{ij}t^{il}_{ab}t^{jk}_{cd} + \tfrac{1}{4}t^{ij}_{cd}t^{kl}_{ab}\Big]\bar{g}^{cd}_{kl}\\ &+ \tfrac{1}{2}\mathcal{A}_{ij}t^{il}_{ab}\bar{V}^{mn}_{kl}c^{jk}_{mn} + \tfrac{1}{4}t^{kl}_{ab}\bar{V}^{mn}_{kl}c^{ij}_{mn},\end{aligned} \tag{90}$$

where:

$$\bar{V}^{mn}_{kl} = \tfrac{1}{2}\bar{g}^{\alpha\beta}_{kl}\bar{R}^{mn}_{\alpha\beta} \approx \Delta^{mn}_{kl} - \tfrac{1}{2}\bar{g}^{oo'}_{kl}\bar{r}^{mn}_{oo'}. \tag{91}$$

The quadratic term to the r_{12} amplitude equation is:

$$\begin{aligned}Q^{ij}_{kl} = &\tfrac{1}{8}\bar{R}^{\alpha\beta}_{kl}\mathcal{A}_{\alpha\beta}\Big(c^{in}_{mm'}\bar{R}^{mm'}_{\alpha\gamma}\bar{R}^{oo'}_{\beta\delta}c^{jn'}_{oo'} + \tfrac{1}{2}c^{ij}_{mm'}\bar{R}^{mm'}_{\alpha\delta}\bar{R}^{oo'}_{\beta\gamma}c^{nn'}_{oo'}\Big)\bar{g}^{\gamma\delta}_{nn'}\\ &+ \tfrac{1}{4}\mathcal{A}_{ij}\bar{X}^{oo'}_{kl}c^{im'}_{oo'}\Big(\bar{V}^{nn'}_{mm'}c^{jm}_{nn'} + \bar{g}^{cd}_{mm'}t^{jm}_{cd}\Big)\\ &+ \tfrac{1}{8}\bar{X}^{oo'}_{kl}c^{mm'}_{oo'}\Big(\bar{V}^{nn'}_{mm'}c^{ij}_{nn'} + \bar{g}^{cd}_{mm'}t^{ij}_{cd}\Big),\end{aligned} \tag{92}$$

which by virtue of the standard approximation, that is, by inserting the resolution of the identity, simplifies to:

$$\begin{aligned}Q^{ij}_{kl} \approx &\tfrac{1}{4}\mathcal{A}_{ij}\bar{X}^{oo'}_{kl}c^{im'}_{oo'}\Big(\bar{V}^{nn'}_{mm'}c^{jm}_{nn'} + \bar{g}^{cd}_{mm'}t^{jm}_{cd}\Big)\\ &+ \tfrac{1}{8}\bar{X}^{oo'}_{kl}c^{mm'}_{oo'}\Big(\bar{V}^{nn'}_{mm'}c^{ij}_{nn'} + \bar{g}^{cd}_{mm'}t^{ij}_{cd}\Big).\end{aligned} \tag{93}$$

The terms that vanish due to the standard approximation are the nonfactorizable Q-term diagrams that involve five-electron integrals. Hence, the FCCD-R12 and CCD-R12 methods do not differ in their r_{12} parts but only in the conventional nonfactorizable quadratic terms.

The reader is referred to recent reviews of R12 theory for further details[23,100].

9.1 Expansion of r_{12} in terms of Gaussian geminals

Persson and Taylor[101] have suggested to expand the linear r_{12} terms in a basis of Gaussian geminals. The linear r_{12} terms introduced in the preceding section can subsequently be replaced by this expansion, with the advantage that the many-electron integrals become tractable. Persson and Taylor studied fits of the type:

$$r_{12} \approx \sum_{v=1}^{N} b_v \left[1 - \exp(-\gamma_v r_{12}^2) \right] \equiv s(12), \tag{94}$$

where the notation $s(12)$ has been introduced to highlight the fact that the r.h.s of (94) is some particular multiplicative two-electron operator. Hence, the theory of explicitly correlated wavefunctions with terms linear in r_{12} can be used with no or minor modifications by replacing the ansatz (69) by:

$$T_2 = \tfrac{1}{8} c_{kl}^{ij} \bar{S}_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta} + \tfrac{1}{4} t_{ab}^{ij} a_{ij}^{ab}, \tag{95}$$

where:

$$\bar{S}_{\mu\nu}^{kl} = \langle \mu\nu | Q(12)\, s(12) \, | kl \rangle. \tag{96}$$

The analogy with fitting Slater-type orbitals (STO) as expansions in Gaussian orbitals is obvious. As for the STO-fits, the main objective of the present approach is to simplify (or make possible) the evaluation of many-electron integrals. Persson and Taylor investigated even-tempered sets of Gaussian geminals of the type $\gamma_v = a_N \, 3^{v-1}$ and obtained very satisfying exponentionally weighted linear least-squares fits of r_{12} with six ($a_6 = 0.111111$) or nine terms ($a_9 = 0.037037$) by minimizing:

$$\chi^2 = \int_0^\infty e^{-2x} \left[x - \sum_{v=1}^{N} b_v (1 - e^{-\gamma_v x^2}) \right]^2 dx. \tag{97}$$

(Actually, Persson and Taylor did not integrate from 0 to ∞, but over a preselected range, for example from 0 to 2, 5, 10, or 15 a_0.) The corresponding fits are shown in Figure 7. Clearly, these expansions will approach a constant value for $r_{12} \to \infty$, but this does not matter since the purpose of the terms is to describe the short-range correlation effects for small r_{12}. For large interelectronic distances, a constant or linearly growing r_{12} term is in fact not desirable and in this respect the correlating functions $s(12)$ are not necessarily inferiour to the linear r_{12} terms. Although the expansions do not describe the cusp for $r_{12} = 0$ (which can not be seen in Figure 7 on the present scale), it has been observed that electron correlation effects are very effectively recovered by these functions[101]. The expansion in Gaussian geminals might perhaps not – or not so efficiently – speed up the convergence in the asymptotic region where the objective is the compute 99% of the correlation

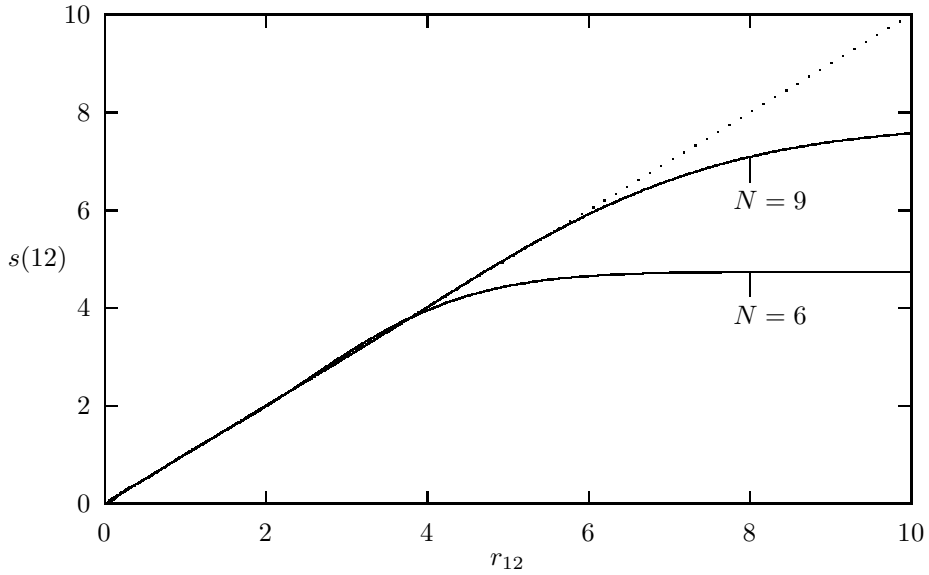

Figure 7. Fits of r_{12} as expansions in terms of six and nine even-tempered Gaussian geminals.

energy or more, but appears to recover a significant part of the correlation energy when used with small or medium-sized basis sets (i.e., basis sets that recover roughly 70–80% of the correlation energy).

Furthermore, it was realized that the even-tempered basis of Gaussian-type geminals could also be applied in the uncontracted form:

$$T_2 = \tfrac{1}{8} \sum_{v=1}^{N} (c_v)_{kl}^{ij} (\bar{S_v})_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta} + \tfrac{1}{4} t_{ab}^{ij} a_{ij}^{ab}, \tag{98}$$

where:

$$(\bar{S_v})_{\mu\nu}^{kl} = \langle \mu\nu | Q(12) \, \exp(-\gamma_v r_{12}^2) \, | kl \rangle. \tag{99}$$

Some initial calculations were performed on He, and it was observed that the variationally determined linear parameters for the Gaussian geminals in (98) were quite similar to the coefficients obtained from the fitting procedure. Results for Ne and H_2O obtained from this (uncontracted) ansatz are presented in Table 6. For the practical calculations in Table 6, the sum over ij and kl in (98) was restricted to the diagonal terms where $ij = kl$ while the occupied orbitals in the integral (99) were expressed in terms of a very small AO basis set (e.g., by one single AO of the total set). This was done for technical reasons. The results nevertheless show that augmentation of standard basis sets with a few explicitly correlated Gaussian geminals improves the percentage of the correlation energy recovered by the basis set from about 73–85 % to ca. 92–98 %.

If the approximations of the linear R12 theory would be exploited in the Persson-Taylor geminals approach (which was not done in their work), not much would

Table 6. MP2(FC) correlation energy (in mE_h) for Ne and H_2O obtained by Persson and Taylor[101] from augmentation of standard orbital basis sets with six Gaussian-type geminals.

		Orbital basis		+ 6 geminals	
	Basis[a]	E_{corr}	%[b]	E_{corr}	%[c]
Ne	cc-pVTZ(uc)	−273.1	85.3	−314.0	98.1
H_2O	cc-pVDZ	−219.8	73.1	−277.0	92.1

a Using Cartesian Gaussians.
(uc) denotes a fully uncontracted basis set.
b Percentage of the limiting value of −320.2 mE_h.[20,102]
c Percentage of the limiting value of −300.5 mE_h.[20]

be gained. The many-electron integrals of the linear R12 methods are only of the two-electron type, and very easy to compute. However, it will certainly be interesting to further investigate the expansion of r_{12} in terms of geminals if a method is developed where all (or some important) many-electron integrals are computed rigorously. One advantage of this method is that it does not require the optimization of nonlinear parameters.

10 Explicitly correlated Gaussians

Cencek and Rychlewski[103−107] have developed a variational method where the n-electron wavefunction is expanded in a basis $\{\Phi_k\}$ of the form:

$$\Phi_k(12\ldots n) = \mathcal{A}\Big\{\Theta(\sigma_1\sigma_n\ldots\sigma_n)\mathcal{P}_R\Big[G_k^0(12)\prod_{i\rangle 2}^{n} g_k^0(i)\Big]\Big\}, \tag{100}$$

where $\mathcal{A}$ is the usual antisymmetrizer, Θ a proper spin function, and $\mathcal{P}_R$ the symmetry projector onto the irreducible representation R of the molecular point group taking care of the symmetry adaptation. The important point to note is that the n-electron basis functions contain only one geminal:

$$G_k^0(12) \equiv G^0_{\alpha_k,\beta_k,\bar\beta_k,\mathbf{B}_k,\bar{\mathbf{B}}_k}(12) = \exp(-\alpha_k r_{12}^2 - \beta_k r_{1B_k}^2 - \bar\beta_k r_{2\bar B_k}^2), \tag{101}$$

where r_{12} is the interelectronic distance, r_{1B_k} is the distance of electron 1 to center $\mathbf{B}_k$, $r_{2\bar B_k}$ is the distance of electron 2 to center $\bar{\mathbf{B}}_k$, and α_k, β_k, and $\bar\beta_k$ are Gaussian exponents (which to some extent are allowed to be negative as long as the function is square integrable). Thus, one Gaussian geminal contains 9 nonlinear variational parameters (3 exponents and 6 coordinates).

By the choice (100), the complexity of the many-electron integrals for any n-electron system is limited to at most four-electron integrals, which can be evaluated analytically[103].

The nonlinear parameters are considered variational parameters in each individual Φ_k and are optimized on the fly. This means that, for a general n-electron molecular system, an expansion in terms of N basis functions of the type (100) contains $N \times (4n + 1)$ nonlinear parameters.

For the systems studied so far, containing up to four electrons, the Cencek-Rychlewski method has provided variational energies for molecules that are superior to all other variational calculations, including the Kołos-Wolniewicz-type calculations for H_2. This success can be attributed to the rigorous and efficient optimization of the nonlinear parameters. Note that the Gaussian centers are not restricted to the positions of the nuclei, but are completely free to float.

Equation (100) is restricted to Gaussian functions with only one single geminal depending on only one single interparticle distance. In later calculations by the authors of the ECG method, however, explicitly correlated Gaussians have been introduced that depend on the interparticle distances of all electrons in the system. For example, spatial basis functions of the form:

$$\Phi_k(1\ldots4) = \exp\left(-\sum_{i=1}^{4}\alpha_{i,k}|\mathbf{r}_i - \mathbf{C}_{i,k}|^2 - \sum_{i=1}^{3}\sum_{j=i+1}^{4}\beta_{ij,k}r_{ij}^2\right) \tag{102}$$

have been employed in calculations on four-electron systems[106,107].

11 Similarity transformed Hamiltonians

In about 1969 the "transcorrelated method" of Boys and Handy[108−116] appeared to be an interesting alternative to the standard methods of numerical quantum chemistry employing explicitly correlated functions. Boys and Handy proposed to consider the non-Hermitian Hamiltonian:

$$\tilde{H}_C = e^{-C}He^{C}, \quad \text{with} \quad C = \sum_{i\langle j} f(\mathbf{r}_i, \mathbf{r}_j). \tag{103}$$

This similarity transformed Hamiltonian only contains three-electron operators, since the Hausdorff expansion

$$\tilde{H}_C = H + [H, C] + \frac{1}{2}[[H, C], C] + \ldots \tag{104}$$

breaks off after the double commutator. Introducing the short-hand notation $f_{ij} \equiv f(\mathbf{r}_i, \mathbf{r}_j)$ and assuming that the correlation factor C is symmetrical ($f_{ij} = f_{ji}$), we find that:

$$[H, C] = -\frac{1}{2}\sum_i\sum_{j\neq i}(\Delta_i f_{ij} + 2\nabla_i f_{ij}\cdot\nabla_i), \tag{105}$$

$$\frac{1}{2}[[H, C], C] = -\frac{1}{2}\sum_i\sum_{j\neq i}\sum_{k\neq i}\nabla_i f_{ij}\cdot\nabla_i f_{ik}. \tag{106}$$

The double commutator is a three-electron operator that commutes with C.

As an example of the similarity transformed Hamiltonian, consider the correlating function $C = f(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}r_{12}$ for the He atom. With this C, it follows that

$$[H, C] = -\frac{1}{r_{12}} - \frac{1}{2}\frac{\mathbf{r}_{12}}{r_{12}}\cdot(\nabla_1 - \nabla_2), \quad \frac{1}{2}[[H, C], C] = -\frac{1}{4}, \tag{107}$$

Table 7. He ground state energies from the similarity transformed Hamiltonian.

	$\exp(-\frac{1}{2}r_{12})H\exp(\frac{1}{2}r_{12})$		Configuration Interaction	
Basis	E/E_h	$\delta E^a/\mathrm{m}E_\mathrm{h}$	E/E_h	$\delta E^a/\mathrm{m}E_\mathrm{h}$
11s	−3.010 759 3	−107.035	−2.879 009 2	24.715
11s8p	−2.904 819 1	−1.095	−2.900 486 5	3.238
11s8p7d	−2.904 048 7	−0.324	−2.902 725 3	0.999
11s8p7d6f	−2.903 793 4	−0.069	−2.903 262 1	0.462
11s8p7d6f5g	−2.903 741 1	−0.017	−2.903 427 2	0.297
11s8p7d6f5g4h	−2.903 729 6	−0.005	−2.903 468 2	0.256

a Error with respect to the exact value of $E = -2.903\,724\,377\ E_\mathrm{h}$.[117]

and the transformed Hamiltonian becomes

$$\tilde{H}_C = h_1 + h_2 - \frac{1}{2}\frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2) - \frac{1}{4}. \tag{108}$$

Since the partial-wave expansion of the operator $U_{12} = -\frac{1}{2}\frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2)$ converges rapidly[87], good convergence of the computed energy with respect to the maximum angular momentum quantum number L_max contained in the basis can be expected. Some preliminary results from the ansatz

$$\Psi = \sum_{pq} c_{pq}\Phi_{pq}, \quad \Phi_{pq} = |\varphi_p(\mathbf{r}_1)\varphi_q(\mathbf{r}_2)|, \tag{109}$$

$$\langle \frac{\partial \Psi}{\partial c_{pq}} | \tilde{H}_C - E | \Psi \rangle = 0, \quad E = \langle \Psi | \tilde{H}_C | \Psi \rangle, \tag{110}$$

are presented in Table 7. The orbitals φ_p were expanded in a Gaussian basis of the type 11s8p7d6f5g4h, which was derived from the 11s8p6d5f4g3h basis used in earlier work on the He dimer[20]. (This 11s8p6d5f4g3h set was augmented with sets of d-, f-, g-, and h-type functions with exponents 22.841124, 10.566783, 4.95893, and 2.39464, respectively.) The results of Table 7 look promising, and it seems worthwhile to reinvestigate the Boys-Handy method (or other explicitly correlated similarity transformed effective Hamiltonians) in the framework of modern coupled-cluster theory[118]. Note that the correlation function $\exp(C)$ was only multiplied with one single determinant in the original Boys-Handy method.

12 MP2-limit corrections

MP2 calculations are computationally less demanding than high-order electron-correlation treatments such as MP4(SDTQ) perturbation theory or the CCSD(T) approach. Therefore, it will often be easier to determine the basis-set error at the MP2 level than at some higher level, and we may ask ourselves whether the MP2 basis-set error could be transferred in an easy way to that higher level.

Suppose we have available the correlation energy or correlation contribution to some molecular property at a given method/basis level of theory, which we denote

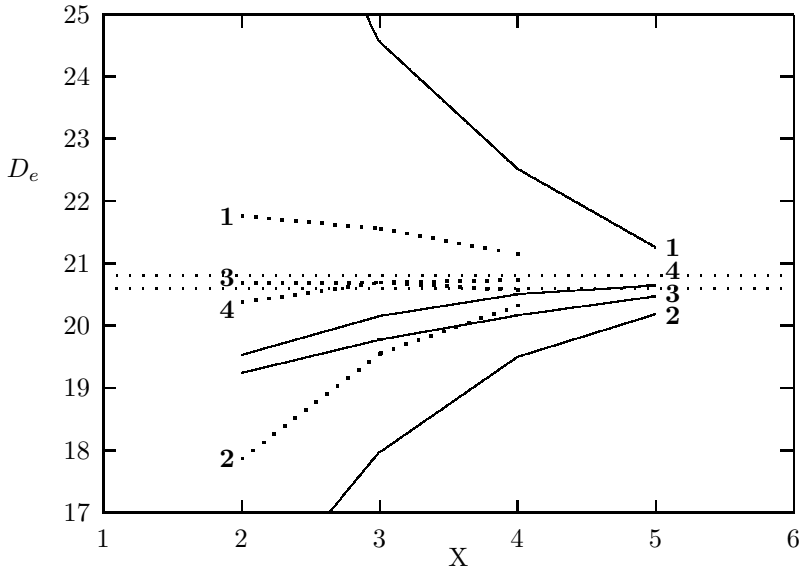

Figure 8. Equilibrium dissociation energy (D_e in kJ mol^{-1}) of the H_2O dimer in the fixed Halkier geometry[41]. The (valence only) unscaled MP2-limit correction is applied to CCSD(T)(FC)/cc-pVXZ (solid lines) and CCSD(T)(FC)/aug-cc-pVXZ (dashed lines) results. Meaning of the curves: **1** = no-CP, no-MP2-limit; **2** = CP, no-MP2-limit; **3** = no-CP, MP2-limit; **4** = CP, MP2-limit.

as Δ(method/basis), and also the corresponding correlation part at the MP2 level in a (nearly) complete basis, denoted as Δ(MP2/∞). Then, there are two evident choices of how to improve the computed Δ(method/basis) data with the known MP2-limits:

$$\Delta(\text{method}/\infty) \approx \Delta(\text{method/basis}) - \Delta(\text{MP2/basis}) + \Delta(\text{MP2}/\infty), \quad (111)$$

$$\Delta(\text{method}/\infty) \approx \Delta(\text{method/basis}) \times \frac{\Delta(\text{MP2}/\infty)}{\Delta(\text{MP2/basis})}, \quad (112)$$

that is, we can add the Δ(MP2/basis) to Δ(MP2/∞) increment to the high-order results or we can scale the high-order results with the Δ(MP2/basis) to Δ(MP2/∞) ratio.

When the finite basis set is enlarged, the increment (111) will eventually vanish and the ratio (112) will converge to unity. Thus, in both cases, it is guaranteed that the improved – that is, the MP2-limit corrected – results will converge to the true limiting values of the high-order approach.

Figure 8 shows the application of (111) with regard to the interaction energy between two H_2O molecules[43]. The correction has been applied to two series of calculations, namely, calculations with the cc-pVXZ sets and with the aug-cc-pVXZ sets, either with (CP) or without (no-CP) counterpoise correction. It is obvious that the convergence to the limiting value (20.7$\pm$0.1 kJ mol^{-1} in this case) is significantly accelerated by the add-on MP2-limit correction (111). The direct addition of the MP2-limit correction has been applied on several occasions, for example in order

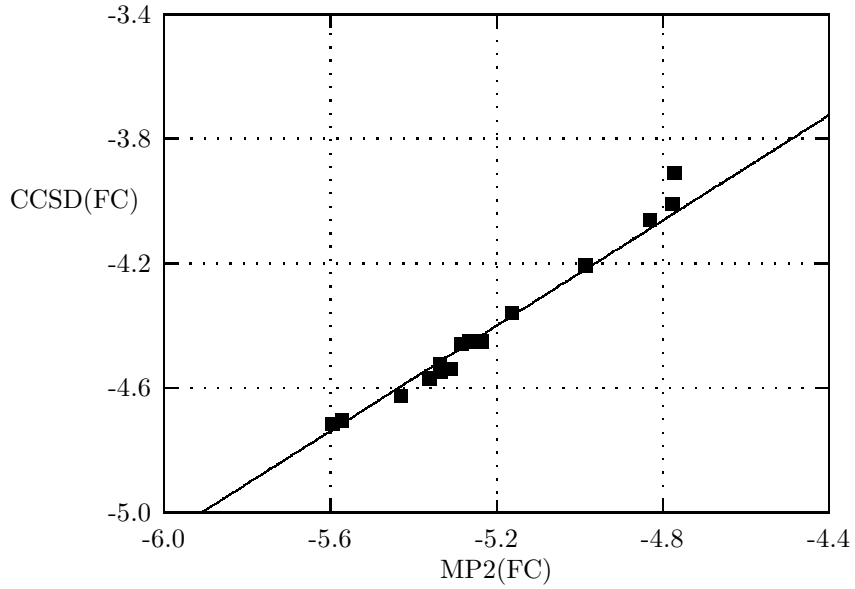

Figure 9. CCSD(FC) correlation contribution versus MP2(FC) correlation contribution to the interaction energy (in kJ mol^{-1}) of the H_2O dimer in the fixed Halkier geometry[41], as obtained from a variety of different basis sets[125].

to obtain accurate results for the ferrocene molecule, the weak benzene$\cdots$neon and benzene$\cdots$argon interactions, and the CO_2 trimer[119−121].

One can argue, however, that the MP2-correlation treatment often overestimates the all-order correlation effects and that, accordingly, the MP2-limit correction for the basis-set error is likely to overestimate the true basis-set error of the high-level method. We have already seen in Section 3.3 that the CBS method utilizes an interference factor to scale down the MP2 basis-set error that was obtained by extrapolation. Also concerning this issue, Van de Bovenkamp and Van Duijneveldt[122] argue that the binding energy of the He dimer as computed by Korona *et al.*[123] (11.06 K) is larger than what is regarded as the limiting value (11.01 K) because Korona *et al.* are believed to have incorrectly combined low-order Gaussian-geminals results with high-order orbital approximations, without taking into account that the low-order Gaussian-geminals corrections give too large contributions.

In view of these difficulties, Martin has proposed to scale the MP2-limit correction Q as follows[124]:

$$\Delta(\text{method}/\infty) \approx \Delta(\text{method/basis}) + Q \times \{\Delta(\text{MP2}/\infty) - \Delta(\text{MP2/basis})\}\,, \quad (113)$$

where Q is computed from the correlation-energy increments from two basis sets at both the MP2 level and the high-level method of interest:

$$Q = \frac{\Delta(\text{method/basis} - \Delta(\text{method/basis}')}{\Delta(\text{MP2/basis} - \Delta(\text{MP2/basis}')}, \quad \text{basis}'\langle\text{basis}. \quad (114)$$

Indeed, it seems a reasonable assumption that the ratio of these increments is

nearly constant for many basis sets beyond some minimum level of accuracy. This is illustrated in Figure 9 for calculations on the H_2O dimer, where CCSD and MP2 correlation contributions to the interaction energy are compared. These correlation contributions have been obtained with various – but all state-of-the-art – basis sets[125]. A nearly linear dependence is found with Q in (113) being the slope of the straight line in Figure 9. Of course, if the ratio of these increments is indeed constant, we can also use[125]:

$$Q = \frac{\Delta(\text{method/basis})}{\Delta(\text{MP2/basis})}. \tag{115}$$

Concerning the H_2O dimer, we can estimate from the results displayed in Figure 9 that the limiting CCSD(FC) correlation contribution is likely to amount to -4.89 kJ mol^{-1} as the valence-only MP2-limit contribution is -5.78 kJ mol^{-1} (cf. Table 4). Adding the SCF (-14.78 kJ mol^{-1}) and (T) triples corrections (-1.05 kJ mol^{-1}) then yields a total CCSD(T)(FC) interaction enery of -20.72 kJ mol^{-1} for the fixed Halkier geometry. Core-correlation effects add -0.14 kJ mol^{-1} and geometry-relaxation effects add -0.12 kJ mol^{-1}. Hence, the total equilibrium binding energy can safely be said to be established to $D_e = 21.0 \pm 0.1$ kJ mol^{-1}.[125]

13 Computational aspects of R12 methods

13.1 Integral-direct implementation

The explicitly correlated methods that rigorously evaluate the many-electron integrals use Gaussian geminals or explicitly correlated Gaussians. The three- and four-electron integrals appearing in the variational method of Cencek and Rychlewski can be computed in closed form[103], while the five-electron integrals appearing in the geminals-based coupled-cluster method are avoided by means of ignoring the corresponding non-factorizable diagrams (FCCD approximation). On the whole, not much is known about the efficient generation of three- and four-electron integrals over Gaussian geminals, but some aspects are discussed by Persson and Taylor[126].

The many-electron integrals over linear r_{12}-dependent functions are more complicated than the integrals over Gaussian geminals, and unfortunately, optimized strategies or algorithms for their computation have not been developed. However, the R12 methods avoid the corresponding three-, four-, and five-electron integrals by virtue of the standard approximations. What remains in the R12 methods are two-electron integrals, some of them special integrals appearing only in the R12 methods.

The algorithms used for the R12 computations have been tailored towards large-scale applications, that is, calculations on molecules with high-quality AO basis sets.

Since the introduction of the integral-direct implementation of the Hartree-Fock method by Almlöf *et al.*[127] in 1982, the integral-direct (or semi-direct) techniques have been refined further and have also been applied to the CCSD level[128–130]. Calculations with more than 500 basis functions are possible at this level today.

The current CCSDT-R12 computer program also employs integral-direct algorithms. In this section, the computational aspects of the implementation that are specific to the CC-R12 approach will be discussed in detail. The notation of Noga and Kutzelnigg[94] is adopted and it is referred to this paper for definitions of the intermediates, integrals, and so forth.

This section will be concerned with the following three R12 related computational tasks: First, the R12 part of the energy, second, the coupling of the R12 functions to the T_1 and T_2 equations, and third, the equation which determines the amplitudes of the r_{12}-type double excitations.

Furthermore, it will be assumed that quantities of the order of N^2 or possibly n^2N^2, where n is the number of occupied orbitals and N is the total number of orbitals, can be kept in the main memory of the computer and can be computed by integral-direct schemes that are analogous to the integral-direct MP2 algorithm (i.e., by an integral-direct partial four-index transformation).

If triple excitations are involved in the method, not only the n^2N^2 quantities, but also the two-electron integrals of the type g_{iq}^{rs} ($\propto nN^3$) are generated by integral-direct techniques. However, these nN^3 quantities are stored on disk.

The R12 contribution to the total CCSD-R12 correlation energy is represented by the diagram on Figure 2d of the paper by Noga and Kutzelnigg[94]. This diagram is evaluated as:

$$E = \tfrac{1}{4} A_{ij}^{kl} c_{kl}^{ij}, \tag{116}$$

where c_{kl}^{ij} are the amplitudes of the r_{12} double replacements, and:

$$A_{kl}^{ij} \approx \Delta_{kl}^{ij} - \frac{1}{2} \bar{r}_{kl}^{pq} \bar{g}_{pq}^{ij}. \tag{117}$$

Except for the numerical value of the amplitudes, this energy expression is identical with the R12 part of the MP2-R12 energy that has been implemented in the integral-direct `SORE` program. It is obvious that the n^2N^2 quantities $\bar{g}_{kl}^{pq}$ and $\bar{r}_{pq}^{ij}$ can be generated by the integral-direct partial four-index transformation, and that the n^4 intermediates A_{kl}^{ij} can be computed using an in-core algorithm.

Whereas only these n^4 intermediates occur in the MP2-R12 method, the higher-order methods also require (although not for the energy) the n^2N^2 intermediates:

$$\bar{V}_{rs}^{ij} = \frac{1}{2} \bar{g}_{rs}^{\alpha\beta} \bar{R}_{\alpha\beta}^{ij} \approx \Delta_{rs}^{ij} - \frac{1}{2} \bar{g}_{rs}^{pq} \bar{r}_{pq}^{ij}. \tag{118}$$

These intermediates, which are computed only once and kept in main memory, are evaluated as follows: In a first step, the $\bar{r}_{pq}^{ij}$ integrals are generated by the integral-direct partial four-index transformation. In a second step, the product $\bar{g}_{rs}^{pq} \bar{r}_{pq}^{ij}$ is computed in full analogy to the "B-term" of conventional integral-direct CC implementations[128,129]:

$$\Omega_{aibj}^{B} = t_{ij}^{cd} \bar{g}_{cd}^{ab}. \tag{119}$$

It is noticed that the integrals $\bar{r}_{pq}^{ij}$ play the role of the amplitudes t_{ij}^{cd} that occur in this B-term.

The new T_1 and T_2 equations of the CCSD-R12 method are easily obtained by modifying the established T_1 and T_2 equations of the traditional CC method

as well as the well-known intermediates F_{mi} and W_{mnij} (for a definition of these intermediates, see for example Equations (4) and (6) in the paper by Stanton *et al.*[131]. Four minor modifications are required. One must add:

$$-\frac{1}{2}\sum_{kl}\sum_{m} c_{kl}^{im}\bar{V}_{ma}^{kl} \qquad \text{to r.h.s. of } T_1 \text{ eq.,} \tag{120}$$

$$\frac{1}{2}\sum_{kl} c_{kl}^{ij}\left(\bar{V}_{ab}^{kl} - \sum_{m} t_b^m \bar{V}_{am}^{kl} + \sum_{m} t_a^m \bar{V}_{bm}^{kl}\right) \qquad \text{to r.h.s. of } T_2 \text{ eq.,} \tag{121}$$

$$\frac{1}{2}\sum_{kl}\sum_{n} c_{kl}^{in}\bar{V}_{mn}^{kl} \qquad \text{to } F_{mi}, \tag{122}$$

$$\frac{1}{2}\sum_{kl} c_{kl}^{ij}\bar{V}_{mn}^{kl} \qquad \text{to } W_{mnij}. \tag{123}$$

The important observation is that only the n^2N^2 quantities $\bar{V}_{rs}^{ij}$ are needed for these modifications. As discussed before, the $\bar{V}_{rs}^{ij}$ intermediates are computed employing integral-direct schemes and stored for later use in the subsequent CCSD-R12 iterations.

For completeness, it is noted that Equation (120) corresponds to diagram d3.15 of the paper by Noga and Kutzelnigg[94], whereas Equation (121) is the sum of the diagrams d4.1 and d4.2. Diagrams d3.16 and d4.5 result from the modified F_{mi} intermediate of Equation (122), and diagrams d4.3 and d4.4 can be traced back to the new W_{mnij} intermediate of Equation (123).

The equation determining the amplitudes of the r_{12} double excitations is given by Equation (III.4) in Table III of the paper by Noga and Kutzelnigg[94]:

$$\begin{aligned}
-\frac{1}{2}\bar{B}_{kl}^{mn}c_{mn}^{ij} = &-\left(\bar{F}_m^j\tilde{\bar{X}}_{kl}^{im} + \bar{F}_m^i\tilde{\bar{X}}_{kl}^{mj}\right) + (\bar{V}^\dagger)_{kl}^{ij} + \frac{1}{2}\bar{G}_{mn}^{ij}\tilde{\bar{X}}_{kl}^{mn} + \frac{1}{2}\bar{P}_{kl}^{mn}c_{mn}^{ij} \\
&+ \frac{1}{2}(\bar{V}^\dagger)_{kl}^{ab}\tau_{ab}^{ij} \; - \frac{1}{2}\left(\bar{Z}_{kl;o}^{mn;j}c_{mn}^{io} + \bar{Z}_{kl;o}^{mn;i}c_{mn}^{oj}\right) \\
&- \frac{1}{2}\left(\bar{Z}_{kl;o}^{mn;a}c_{mn}^{io}t_a^j + \bar{Z}_{kl;o}^{mn;a}c_{mn}^{oj}t_a^i\right) \; + \frac{1}{2}\bar{Z}_{kl;o}^{mn;a}c_{mn}^{ij}t_a^o.
\end{aligned} \tag{124}$$

Inspection of the auxiliary quantities[94] $\bar{F}$, $\tilde{\bar{X}}$, $\bar{V}$, $\bar{G}$, $\bar{P}$, and $\bar{Z}$ reveals that these intermediates only depend on integrals and/or other auxiliary quantities that carry *at least two* occupied indices. Therefore, the constructon and solution of (124) involves only in-core procedures. Recall that n^2N^2 quantities are kept or handled in main memory. For example, consider:

$$\bar{P}_{kl}^{mn} = \frac{1}{4}\bar{R}_{kl}^{\alpha\beta}\bar{g}_{\alpha\beta}^{\gamma\delta}\bar{R}_{\gamma\delta}^{mn} \approx -\frac{1}{2}\bar{r}_{kl}^{pq}\bar{V}_{pq}^{mn}. \tag{125}$$

The computation of $\bar{P}_{kl}^{mn}$ is straightforward as soon as the integrals $\bar{r}_{kl}^{pq}$ and $\bar{V}_{pq}^{mn}$ are available. The only exception is the computation of:

$$\bar{X}_{rs}^{ij} = \frac{1}{2}\bar{R}_{rs}^{\alpha\beta}\bar{R}_{\alpha\beta}^{ij} \approx (\bar{r^2})_{rs}^{ij} - \frac{1}{2}\bar{r}_{rs}^{pq}\bar{r}_{pq}^{ij}, \tag{126}$$

which requires a B-term-like procedure analogous to Equation (118). It is noted that the integral $(\bar{r^2})_{rs}^{ij}$ factorizes into products of one-electron integrals.

Furthermore, a direct MP2-like partial four-index transformation must be performed for the two-electron integrals $\bar{t}_{pq}^{ij}$ over the operators $[T(1), r_{12}]$ and $[T(2), r_{12}]$. These integrals also occur in the direct MP2-R12 program SORE. Notice that the SORE program is based on standard approximation A, which does not involve the quantities $\bar{X}_{rs}^{ij}$, whereas these quantities are required by the standard approximation B based MP2-R12/B method.

The integral-direct procedure to generate the R12 specific auxiliary quantities that are required by the CCSD-R12 method can be summarized as follows: In a first pass through the two-electron integral generator, the integral-direct partial four-index transformation is processed to generate the integrals $\bar{t}_{pq}^{ij}$, $\bar{r}_{pq}^{ij}$, and $\bar{g}_{pq}^{ij}$. This step corresponds to the MP2-R12/A method as implemented in the SORE program. In a second pass, the integral-direct algorithm for the B-term is performed simultaneously with the two-electron integrals over $1/r_{12}$ and r_{12} to obtain the products $\bar{g}_{pq}^{rs}\bar{r}_{rs}^{ij}$ and $\bar{r}_{pq}^{rs}\bar{r}_{rs}^{ij}$, respectively.

For methods that involve triple excitations, an integral-direct scheme to compute the integrals g_{iq}^{rs} is processed and these integrals are stored on disk along with appropriate labels. It is noted that in the present CC-R12 implementation the energy contributions due to triple excitations depend on the R12 basis functions not explicitly, but only indirectly through the R12 induced changes in the amplitudes of the conventional single and double excitations.

In each CCSD-R12 or CCSDT-1a-R12 iteration, the two-electron integrals over $1/r_{12}$ are recomputed to contribute to the integral-direct part of the conventional CC equations. On the other hand, all of the R12 part of the CC equations is computed beforehand, and the computational cost of this part roughly compares with the computational work of just a few (≈ 6) conventional CC iterations.

Hence, an important computational aspect is the generation of the R12 related integrals.

13.2 Two-electron integrals

The linear R12 methods require the computation of four types of two-electron integrals over Cartesian Gaussian functions:

$$(ab|r_{12}^{-1}|cd) = \int\int \psi_a(1)\psi_c(2)\, r_{12}^{-1}\, \psi_b(1)\psi_d(2)\, d\tau_1 d\tau_2, \tag{127}$$

$$(ab|r_{12}|cd) = \int\int \psi_a(1)\psi_c(2)\, r_{12}\, \psi_b(1)\psi_d(2)\, d\tau_1 d\tau_2, \tag{128}$$

$$(ab|[T_1, r_{12}]|cd) = \int\int \psi_a(1)\psi_c(2)\, [T_1, r_{12}]\, \psi_b(1)\psi_d(2)\, d\tau_1 d\tau_2, \tag{129}$$

$$(ab|[T_2, r_{12}]|cd) = \int\int \psi_a(1)\psi_c(2)\, [T_2, r_{12}]\, \psi_b(1)\psi_d(2)\, d\tau_1 d\tau_2. \tag{130}$$

$T_i = -\frac{1}{2}\Delta_i$ is the kinetic energy operator ($i = 1, 2$) and ψ_a, ψ_b, ... are primitive Cartesian Gaussians with exponents a, b, ...,

$$\psi_a(1) = g_{a,\mathbf{A},\mathbf{l}}(1) = N_A x_{1A}^{l_x} y_{1A}^{l_y} z_{1A}^{l_z} \exp(-a r_{1A}^2). \tag{131}$$

This function is centered at $\mathbf{A}$, N_A is a normalization constant, and $x_A = x - A_x$, etc. It has been shown shown that the integral (129) can be computed very

efficiently from the relationship[132]:

$$(ab|[T_1, r_{12}]|cd) = -\left(\frac{a-b}{a+b}\right)(ab|r_{12}^{-1}|cd) - \nabla_P \cdot \nabla_R\,(ab|r_{12}|cd), \tag{132}$$

where the relative coordinates $\mathbf{P}$ and $\mathbf{R}$ are defined by:

$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{a+b} \quad \text{and} \quad \mathbf{R} = \mathbf{A} - \mathbf{B}. \tag{133}$$

The integral (130) can be computed similarly:

$$(ab|[T_2, r_{12}]|cd) = -\left(\frac{c-d}{c+d}\right)(ab|r_{12}^{-1}|cd) - \nabla_Q \cdot \nabla_S\,(ab|r_{12}|cd), \tag{134}$$

where:

$$\mathbf{Q} = \frac{c\mathbf{C} + d\mathbf{D}}{c+d} \quad \text{and} \quad \mathbf{S} = \mathbf{C} - \mathbf{D}. \tag{135}$$

By expanding the Gaussian charge distributions in Hermite functions:

$$\psi_a\psi_b = \sum_{tuv} E_{tuv}^{ab}\Lambda_{tuv}, \tag{136}$$

$$\Lambda_{tuv}(\mathbf{r}, p, \mathbf{P}) = \left(\frac{\partial}{\partial P_x}\right)^t \left(\frac{\partial}{\partial P_y}\right)^u \left(\frac{\partial}{\partial P_z}\right)^v \exp(-pr_P^2), \tag{137}$$

(with $p = a + b$), the integrals can be obtained from:

$$(ab|r_{12}^{-1}|cd) = \sum_{t'u'v'} E_{t'u'v'}^{cd} \sum_{tuv} E_{tuv}^{ab}(tuv|r_{12}^{-1}|t'u'v'), \tag{138}$$

$$(ab|r_{12}|cd) = \sum_{t'u'v'} E_{t'u'v'}^{cd} \sum_{tuv} E_{tuv}^{ab}(tuv|r_{12}|t'u'v'). \tag{139}$$

The integral over $[T_1, r_{12}]$ can be computed from:

$$\begin{aligned}(ab|[T_1, r_{12}]|cd) = &-\left(\tfrac{a-b}{a+b}\right)\textstyle\sum_{t'u'v'} E_{t'u'v'}^{cd} \sum_{tuv} E_{tuv}^{ab}(tuv|r_{12}^{-1}|t'u'v') \\ -\textstyle\sum_{t'u'v'} E_{t'u'v'}^{cd} \sum_{tuv} &\Big\{E_{tuv}^{ab;x}(t{+}1, uv|r_{12}|t'u'v') + E_{tuv}^{ab;y}(t, u{+}1, v|r_{12}|t'u'v') \\ &+ E_{tuv}^{ab;z}(tu, v{+}1|r_{12}|t'u'v')\Big\}.\end{aligned} \tag{140}$$

Here it was used that:

$$\frac{\partial}{\partial P_x}(tuv|r_{12}|t'u'v') = (t{+}1, uv|r_{12}|t'u'v'), \tag{141}$$

$$E_{tuv}^{ab;x} = \frac{\partial}{\partial R_x} E_{tuv}^{ab}. \tag{142}$$

The integral $[T_2, r_{12}]$ can be computed analogously. By virtue of the change of variables to relative coordinates, the range of summation over t, u, and v is the same for all types of integrals. But note that the range of intermediate integrals over Hermite functions has been increased by one "quantum" due to the differentiation with respect to P_x (P_y, P_z) or Q_x (Q_y, Q_z). Furthermore, it has been shown that the integrals $(tuv|r_{12}|t'u'v')$ over Hermite functions can be obtained from the

electron-repulsion integrals $(tuv|r_{12}^{-1}|t'u'v')$ with negligible computational cost[132]. As an overall result, the computational effort required for the evaluation of the four types of two-electron integrals occuring in the R12 methods is roughly equal to four times the effort for the computation of the usual electron-repulsion integrals alone.

A recent development has been concerned with the computation of the $[T_1, r_{12}]$ and $[T_2, r_{12}]$ integrals at a later stage of the four-index transformation of the integrals from the atomic orbital (AO) basis into the orthonormal Hartree-Fock molecular orbital (MO) basis[133]: It was suggested to exploit the relation:

$$\begin{aligned}(ab|[T_1, r_{12}]|JQ) = &-\left(\tfrac{a-b}{a+b}\right)\sum_{tuv} E^{ab}_{tuv}(tuv|r_{12}^{-1}|JQ)\\ -\sum_{tuv}&\Big\{E^{ab;x}_{tuv}(t{+}1, uv|r_{12}|JQ) + E^{ab;y}_{tuv}(t, u{+}1, v|r_{12}|JQ)\\ &+E^{ab;z}_{tuv}(tu, v{+}1|r_{12}|JQ)\Big\}, \end{aligned} \tag{143}$$

where J and Q are MOs (J occupied, Q arbitrary), and simularly for the integral $(IP|[T_2, r_{12}]|cd)$. In the proposed algorithm, the Hermite integrals are transformed partially into the MO basis before the final $[T_1, r_{12}]$ and $[T_2, r_{12}]$ integrals are assembled. Since the number of occupied orbitals is relatively small (i.e., much smaller than the size of the AO basis), the new scheme based on (143) seems very attractive. At this point it is noted that the coupled-cluster R12 methods require exactly the same transformed MO integrals of the type $(IP|[T_1, r_{12}]|JQ)$ and $(IP|[T_2, r_{12}]|JQ)$, such that the CC-R12 methods will be improved to the same extent.

The performance of the R12 integral generation and corresponding four-index transformation is illustrated in Table 8. Shown are the timings for MP2-R12/A calculations on ferrocene and the permanganate ion. Remember that these MP2-R12/A calculations implicitly generate the transformed $[T(1), r_{12}]$ and $[T(2), r_{12}]$ integrals required by the CC-R12 methods, in other words, that the extra work in CC-R12 calculations compared with conventional coupled-cluster calculations in a good approximation consists of the computational steps displayed in Table 8. The computation time needed for the evaluation of the two-electron integrals for the ferrocene molecule might seem somewhat high: 1100 minutes. This is due to the fact that four passes through the program were needed as not more than ca. 15 gigabytes of external storage were available for the partially transformed integrals.

In summarizing, it is concluded that interesting applications of the R12 methods are possible today and will be even more so in the future due to the efficient atomic orbital driven direct implementations of the two-electron integrals in the MP2-R12 and CC-R12 computer programs.

14 Numerical examples

Today, explicitly correlated calculations can be performed on transition metal compounds. To illustrate that this type of calculations is not confined to small two- or four-electron systems (ten-electron sytems at the best), Table 9 shows the optimized structures of ferrocene ($Fe(C_5H_5)_2$ or $Fe(Cp)_2$ for short) and the permanganate ion (MnO_4^-) as obtained from MP2-R12/A calculations. For ferrocene, only the distance from Fe to the center of mass of the cyclopentadienyl ring was opti-

Table 8. Performance assessment of the SORE program, obtained from calculations on $FeCp_2$ and MnO_4^- on a NEC SX-3/24R supercomputer.

	$FeCp_2$ [a]		MnO_4^- [b]	
	t_{cpu}/min[c]	GFLOPS[d]	t_{cpu}/min[c]	GFLOPS[d]
Integrals				
Evaluation	1100	0.5	53	0.6
Sorting	75	–	5	–
Transformation				
1^{st} step	48	3.0	6	3.7
2^{nd} step	41	5.1	7	5.5
3^{rd} step	10	1.3	2	1.3
4^{th} step	20	0.3	2	0.3
Miscellaneous[e]	97	≈ 0	10	≈ 0
Total	1391	0.7	85	1.1

a Exploiting D_{5d} symmetry, correlating 66 electrons, and using 864 basis functions. The calculation required 4×12 gigabytes of disk space, the mean vector length was 176 elements, and the degree of vectorization was 96.4%.

b Exploiting T_d symmetry, correlating 40 electrons, and using 520 basis functions. The calculation required 15 gigabytes of disk space, the mean vector length was 192 elements, and the degree of vectorization was 97.6%.

c Central processor unit (cpu) time in minutes.

d 1 GFLOPS = 1×10^9 floating point operations per second.

e Consists mainly of the computation time required for the computation of the MP2-R12/A energy. This part of the calculation has not been vectorized.

Table 9. Fe–Cp and Mn–O bond lengths (in pm) of the ferrocene molecule and the permanganate ion, computed at the basis set limit of second-order perturbation theory[a].

Molecule	Basis	N^b	$n_e{}^c$	SCF	MP2[d]	Experiment
$Fe(Cp)_2$	Fe:16s12p8d6f/ C:8s5p4d3f/H:3s2p	864	66 58	187.2	146.8 148.1	166.1 ± 0.4[e]
MnO_4^-	Mn:17s13p10d6f/ O:13s9p5d4f	520	40	154.3	158.1	162.9 ± 0.8[f]

a Obtained from MP2-R12/A (SORE) calculations.

b Number of basis functions.

c Number of electrons correlated.

d K-shells and L-shell of transition metal not correlated.

e Gas-phase bond-distance as reported by Haaland[134].

f Crystal structure of $KMnO_4$ determined by Palenik[135].

mized. The basis set for ferrocene is described elsewhere[120], while the basis set for MnO_4^- was derived from the ANO basis sets of Widmark *et al.*[136] and Pou-Amérigo

Table 10. Bond disruption enthalpy (ΔH°_{298} in kJ mol^{-1}) of ferrocene computed from the heterolytic dissociation: $FeCp_2 \rightarrow Fe^{2+}(^5D) + 2\,Cp^-$.

CCSD(T)	CASPT2	Method/Basis set	N^a	$n_e{}^b$
3 046		CCSD(T)/TZV2P+f[c]	373	66
	3 117	CASPT2/basis 4[c,d]	255	58
+42	−42	MP2-R12/A correction[e]	865	58&66
+8	+38	Other corrections[f]		
3 096	3 114			
−363	−363	$\Delta E(^1I–^5D)$ excitation energy [145]		
2 733	2 751	Theoretical ΔH°_{298}		
2 742 ± 60		Best estimate		
2 658 ± 26		Experimental value[146]		

a Number of contracted basis functions.

b Numer of electrons correlated.

c With respect to the ^1I state of Fe^{2+}.

d Basis 4 = Fe:6s5p4d2f/C:4s3p1d/H:2s.

e Using the basis set Fe:16s12p8d6f/C:13s7p4d3f/H:6s2p.

f Semicore 3s3p correlation, vibrational zero-point energy, translational, rotational, and vibrational thermal energy, structural relaxation, and relativistic corrections.

et al.[137] (The spdf part of the primitive 21s15p10d6f4g set for Mn was contracted to a segmented contraction of the type 17s13p10d6f by contracting the innermost orbitals. Similarly, the primitive 14s9p4d3f set for O was contracted to a segmented contraction of the type 11s7p4d3f and diffuse functions (2s2p1d1f) were added to the latter by geometrical progression.) The results in Table 9 represent the AO basis set limit results for the SCF and MP2 levels of theory and can be used to calibrate standard one-particle basis sets for transition metal compounds at the Hartree-Fock and correlated levels. For example, the present Fe–Cp bond length at the MP2 level (correlating 66 electrons) is ca. 11 pm shorter than the MP2 value of 158 pm obtained by Park and Almlöf[138] – indicating serious basis set deficiencies in their calculations – while the present limiting value of 148.1 pm (correlating 58 electrons) agrees well with the MP2 result of 148.6 pm obtained by Pierloot *et al.*[139]

The benchmark calculations on MnO_4^- were performed to calibrate basis sets for future theoretical studies of the electronic spectrum. Such studies using density functional, symmetry-adapted-cluster CI (SAC-CI), and coupled-cluster theory have been performed by Dickson and Ziegler[140], Nakai *et al.*[141,142], and Nooijen[143], respectively. For both ferrocene and permanganate, it is interesting to investigate how well single-reference based coupled-cluster methods perform despite the well-known Hartree-Fock failure for these transition metal compounds.

Recent complete active space self-consistent-field (CASSCF), complete active space second-order perturbation theory (CASPT2), and coupled-cluster calculations using large Gaussian basis sets were concerned with the molecular structure and binding energy of ferrocene[139,144].

Koch *et al.*[144] determined the equilibrium bond length to $R_{Fe-Cp} = 166.0$ pm,

in full agreement with the experimental value, and reported the total CCSD(T) energy of ferrocene obtained from calculations using a large Gaussian basis set containing 373 contracted basis functions. These authors correlated all 66 valence electrons.

Pierloot *et al.*[139], using an active space consisting of 10 electrons distributed among 10 orbitals and a basis set containing 255 functions, obtained a bond length of $R_{\mathrm{Fe-Cp}} = 164.3$ pm at the counterpoise corrected CASPT2 level correlating 58 electrons (i.e., freezing the 3s/3p semicore orbitals of Fe). They also computed the bond disruption enthalpy from the heterolytic dissociation

$$\mathrm{FeCp_2} \rightarrow \mathrm{Fe^{2+}}(^5\mathrm{D}) + 2\mathrm{Cp^-},$$

which amounted to 2 628 kJ mol^{-1} at the CASPT2 level, in good agreement with the experimental value of $2\,658 \pm 26$ kJ mol^{-1}.[146]

MP2-R12/A calculations were performed to obtain insight into the remaining errors in the CCSD(T) and CASPT2 calculations related to the use of a finite AO basis set[120]. These MP2-R12/A calculations were performed with a large Gaussian basis set of the type Fe:16s12p8d6f/C:13s7p4d3f/H:6s2p containing more than 1000 Cartesian Gaussian functions. Furthermore, core and core-valence correlation effects as well as thermal, vibrational, relativistic, and structural relaxation effects were studied[120].

The results of this study are presented in Table 10. The CCSD(T) and CASPT2 calculations used very different basis sets, and hence, the MP2-R12/A complete basis set corrections differ largely. However, the two corresponding extrapolations of the theoretical bond disruption enthalpy are very similar, and the deduced averaged value amounts to $2\,742 \pm 60$ kJ mol^{-1}. This is the currently most accurate theoretical estimate. The agreement of this estimate with the experimental value is not satisfactory and the latter is challenged by the *ab initio* calculations. To resolve the disagreement in more detail, future studies of the individual heats of formation of ferrocene, $\mathrm{Fe^{2+}}$, and $\mathrm{Cp^-}$ are required. Especially for $\mathrm{Cp^-}$, the experimental value might be uncertain.

15 Concluding remark

In the present lecture, we have seen how the poor description of the Coulomb cusp leads to a very poor basis-set convergence of the orbital approximation to the electron correlation problem. Wavefunctions with explicit depence on the interelectronic coordinates r_{ij} help to overcome the poor convergence. One can add the r_{ij}-dependent terms to the wavefunction or transform the Hamiltonian accordingly.

There are, still, a few more approaches that aim at quantitatively correct computations of electron correlation effects. One could for example employ quantum Monte Carlo methods[147] or integrate the correlation energy functional with the Hartree-Fock density if that functional were known to high accuracy[148]. Another set of techniques, including extrapolation, scaling, and empirical corrections can be found among the Gn ($n = 1, 2, 3$) family of methods[149]. Cf. the paper by Curtiss *et al.*[149] for more references. We have not discussed these alternative methods as the focus of the present lecture was on R12 methods and Gaussian geminals.

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